THE

ASTROPHYSICAL JOURNAL

AN INTERNATIONAL REVIEW OF SPECTROSCOPY
AND ASTRONOMICAL PHYSICS

VOLUME XVIII SEPTEMBER 1903 NUMBER 2

ON MEASUREMENTS OF WAVE-LENGTH WITH THE CONCAVE GRATING OBJECTIVE SPECTROSCOPE.

By F. L. O. WADSWORTH.

IN a recent paper[1] I have investigated the question of the aberration which is introduced by the use of the concave grating as a direct objective spectroscope. It was found that for all points not exactly on the axis of the grating the aberration was different in nature, and, in most cases, very much greater in amount than that produced by using the grating in the manner proposed and adopted by Rowland. The question of the effect of this increased unsymmetrical aberration on the size of the field of good definition and on the accuracy of measurement of wave-lengths with the instrument were very briefly discussed in the paper to which reference has been made and in a second paper, "On the Optical Conditions Required to Secure Maximum Accuracy of Measurement in the Use of the Telescope and Spectroscope," published in preceding numbers of this JOURNAL.[2]

[1] "On the Aberration of a Concave Grating when Used as an Objective Spectroscope," *Phil. Mag.*, (6) **6**, 119–156, July 1903.

[2] **16**, 267–299; **17**, 1–19, 100–133, 163; See particularly pp. 285–288 (note errata on p. 287 as corrected in **17**, 163).

The theory and method of using the concave grating as an objective spectroscope was first published by the writer in 1896.[1] Since then it has been used in this way by a number of investigators, among whom may be mentioned Poor, Mitchell, Frost, Mohler and Daniel, and Jewell and Humphreys. It was used by the writer in 1900 at Union Springs, Alabama, in photographing the flash spectrum and coronal rings during the total solar eclipse of May 28.[2] The unsatisfactory results yielded by the preliminary examination of the plates then obtained led me to the more detailed investigation of the aberration of the instrument; and the conclusions reached indicate that both as a spectrograph and as a spectrometer the concave grating objective spectroscope is far below the standard of the objective prism and the plane grating objective spectroscope. In the case of our own plates the errors of displacement of the lines are so large and the definition at the edges of the field so imperfect that I have not considered the results of wave-length measurement that might be obtained from them worthy of comparison with those determined by other parties with the slit, objective prism, and plane grating objective spectrographs.[3] This bad definition and lack of accuracy is in part due, in our case, to the very large angular aperture employed (with the view of securing great rapidity), and in part to the method of mounting adopted (also with a specific object). This, as I have since found by the mathematical investigation, is less favorable than another form would have been.

Other observers who have used the instrument in eclipse work also report unfavorably[4] as to the performance of the instrument, but ascribe the poor results either to the use of improper plates or to defects in the focusing. While these causes may have operated to contribute to the difficulties, they

[1] ASTROPHYSICAL JOURNAL, **3**, 54–60, January 1896.

[2] *Report of the Director of the Allegheny Observatory for 1900*, pp. 23–24 (9). Also "Account of Allegheny Observatory Eclipse Expedition," S. M. KINTNER, *Western University Courant*, **15**, 266–270.

[3] See also footnote on p. 87.

[4] See for example FROST, ASTROPHYSICAL JOURNAL, **12**, 85, 307; MOHLER and DANIEL, *ibid.*, **12**, 361 and HUMPHREYS, *ibid.*, **16**, 313.

are not, as it now appears, the chief sources of error. The latter are to be found in the inherent optical defects of the instrument itself.

The general expression for the aberration in the primary plane of a concave grating when used as an objective spectroscope is, as has been already found,[1]

$$\begin{aligned} Z &= -\frac{\rho}{2}\sin^3\beta\sin\theta\cos i\frac{(\cos i+\cos\theta)}{\cos^2\theta} \\ &\quad +\frac{\rho}{8}\sin^4\beta\frac{\cos i+\cos\theta}{\cos^2\theta}[\cos^2 i-(\cos\theta+2\cos i)^2\,\mathrm{tang}^2\theta] \qquad (1) \\ &= -U+S, \end{aligned}$$

where ρ is the radius of curvature of the grating surface, β is the semi-angular aperture measured at the center of curvature, and i and θ are the angles of incidence and diffraction respectively. Both β and θ are measured positively to the right from the normal to the grating (viewed from the center of curvature), while i is measured positively to the left of this axis. The nature and numerical value of the aberration depends both on the dimensions and optical constants of the grating and on the form of mounting adopted for the instrument. As described in a previous paper, there are four general types of mounting that may be employed, and these have been designated respectively as A–B, C–D, E–F, and G–H.

In the solar eclipse work with which we are now dealing only two of these types have been used; *i.e.*, the A–B type by Frost, Mohler and Daniel, and Jewell and Humphreys, and the G–H type by the writer. The dimensions and other optical constants of the four gratings and the positions in which they were used are given in Table I. The aberrations at the centers and the edges of the photographic fields, computed from the data in Table I by the aid of (1), are tabulated in Table II.

In order to determine the effect of a given amount of aberration, Z, on the form and position of the spectral image at different parts of the field we must find how the distribution in intensity in the diffraction pattern at the focal plane is affected by the unsymmetrical constituent U and the symmetrical constit-

[1] *Phil. Mag.*, **6**, 124, July 1903.

TABLE I.

Observer	Grating	Constants of Grating							Position of Use			Field	κ
		ρ	a	$\beta=\frac{a}{2\rho}$	π	$N=n\delta$	r In Tenth meters	ϵ	Mounting	i	θ_0	λ_1 to λ_2	θ_1 to θ_2
		cm	cm			about	about	about					
Frost, Wadesboro, 1900	F.	150	4.4	0.0147	5684	25,000	0.17 0.20	0.01	A-B	15°10′	0°0′	4200 4600 4950	+(1°18′) to −(1° 9′)
Mohler and Daniel, 1900	M.	305	10.0	.0164	5684	57,000	0.08 0.10	0.006	A-B	16°	0°0′	4300 to 5880	+(1°45′) to −(3°25′)
Wadsworth, Union Spgs., 1900	W.	175.3	13.2	.0377	1421	18,750	0.10 0.11	0.007	G H	12°50′	12°50′	5880 3d 000 6270 3d	+(28°15′) to −(2°35′)
Jewell and Humphreys, Fort de Kock, 1901	J.*	915	10.0 2.0	$\beta_1=.0109$ $\beta_2=.0022$	5684	68,200	0.045 0.075	0.003 0.005	A-B	14°50′	0°0′	3100 4500 5200	+(4°34′) to −(2°17′)

TABLE II. Aberrations.

Grating	$\sin^3\beta$	$\frac{1}{2}\rho\sin^3$	$\frac{1}{8}\rho\sin^4\beta$	At Center of Field. λ_0 θ_0					At Right Edge. λ_1 κ_1					At Left Edge. λ_2 κ_2				
				Sym. S.		Unsym. U.			Sym. S.		Unsym. U.			Sym. S.		Unsym. U.		
				10^{-6}	λ	10^{-6}	λ	$d\lambda$	10^{-6}	λ	10^{-6}	λ	$d\lambda$	10^{-6}	λ	10^{-6}	λ	$d\lambda$
F	3.18×10^{-6}	238×10^{-6}	0.88×10^{-6}	1.6	.03	....	....	....	1.6	0.03	10.2	0.24	.04	1.6	0.03	9.02	0.18	.04
M	4.41×10^{-6}	672×10^{-6}	2.75×10^{-6}	4.98	.09	....	....	....	4.9	.09	38.6	.90	.07	4.8	.09	75.6	1.3	.13
W	53.6×10^{-6}	4698×10^{-6}	44.3×10^{-6}	44.3	.80	2087	37	?	−144	2.5	5180	88.0	?	82.6	1.2	408.0	6.8	?
*J β_1	1.29×10^{-6}	590×10^{-6}	1.6×10^{-6}	2.94	.07	....	....	....	2.78	.09	89.6	2.9	.15	2.92	.06	44.7	0.9	.09
J β_2	0.01×10^{-6}	5×10^{-6}	0.00×10^{-6}															

TABLE III.

$\frac{a}{a_0}$	I_0^2	I_u^2 $U=\frac{\lambda}{4}$	$U=\frac{\lambda}{2}$		$U=\frac{3}{4}\lambda$		$U=\lambda$		$U=\frac{7}{4}\lambda$		$U=2\lambda$	
			$\frac{a}{a_0}$	I_u^2	$\frac{a}{a_0}$	I_u^2	$\frac{a}{a_0}$	I_u^2	$\frac{a}{a_0}$	I_u^2	$\frac{a}{a_0}$	I_u^2
−2.0	.0000	.0086	−2.52	.0030	−2.88	.0016	−3.16	.0001	−3.84	.0004	−4.0	.0000
−1.9	.0027	.0081	−2.40	.0026	−2.74	.0009	−3.00	.0000	−3.65	.0001	−3.8	.0001
−1.8	.0108	.0061	−2.27	.0014	−2.59	.0002	−2.84	.0006	−3.46	.0000	−3.6	.0002
−1.7	.0229	.0035	−2.14	.0002	−2.45	.0000	−2.68	.0015	−3.26	.0004	−3.4	.0002
−1.6	.0358	.0012	−2.02	.0001	−2.30	.0005	−2.53	.0020	−3.07	.0008	−3.2	.0000
−1.5	.0450	.0000	−1.89	.0016	−2.16	.0010	−2.37	.0019	−2.88	.0010	−3.0	.0001
−1.4	.0468	.0004	−1.76	.0045	−2.02	.0010	−2.21	.0012	−2.69	.0008	−2.8	.0006
−1.3	.0392	.0018	−1.64	.0081	−1.87	.0004	−2.06	.0005	−2.50	.0004	−2.6	.0014
−1.2	.0243	.0032	−1.51	.0110	−1.73	.0000	−1.90	.0001	−2.30	.0001	−2.4	.0018
−1.1	.0080	.0033	−1.38	.0123	−1.58	.0011	−1.74	.0000	−2.11	.0000	−2.2	.0018
−1.0	.0000	.0018	−1.26	.0125	−1.44	.0049	−1.58	.0001	−1.92	.0002	−2.0	.0015
−0.9	.0119	.0001	−1.14	.0112	−1.30	.0119	−1.42	.0006	−1.73	.0013	−1.8	.0014
−0.8	.0547	.0017	−1.01	.0101	−1.15	.0212	−1.26	.0034	−1.54	.0042	−1.6	.0020
−0.7	.1353	.0125	−0.88	.0099	−1.01	.0313	−1.10	.0112	−1.34	.0101	−1.4	.0041
−0.6	.2545	.0399	−0.76	.0120	−0.86	.0408	−0.95	.0234	−1.15	.0164	−1.2	.0092
−0.5	.4053	.0911	−0.63	.0181	−0.72	.0493	−0.79	.0428	−0.96	.0287	−1.0	.0189
−0.4	.5754	.1714	−0.51	.0323	−0.58	.0579	−0.63	.0672	−0.77	.0388	−0.8	.0337
−0.3	.7368	.2813	−0.38	.0605	−0.43	.0688	−0.48	.0934	−0.58	.0489	−0.6	.0522
−0.2	.8751	.4159	−0.25	.1103	−0.29	.0856	−0.32	.1194	−0.38	.0605	−0.4	.0719
−0.1	.9675	.5640	−0.12	.1886	−0.14	.1128	−0.16	.1440	−0.19	.0764	−0.2	.0910
−0.0	1.0000	.7093	−0.00	.2976	−0.00	.1553	−0.00	.1688	−0.00	.1002	−0.0	.1097
+0.1	.9675	.8326	+0.12	.4312	+0.14	.2178	+0.16	.1966	+0.19	.1348	+0.2	.1302
+0.2	.8751	.9158	+0.25	.5731	+0.29	.3013	+0.32	.2304	+0.38	.1804	+0.4	.1551
+0.3	.7368	.9450	+0.38	.6983	+0.43	.3998	+0.48	.2722	+0.58	.2320	+0.6	.1860
+0.4	.5754	.9137	+0.51	.7790	+0.58	.4984	+0.63	.3205	+0.77	.2784	+0.8	.2208
+0.5	.4053	.8246	+0.63	.7919	+0.72	.5733	+0.79	.3682	+0.96	.3056	+1.0	.2519
+0.6	.2545	.6901	+0.76	.7278	+0.86	.5994	+0.95	.4029	+1.15	.3022	+1.2	.2679
+0.7	.1353	.5287	+0.88	.5951	+1.01	.5592	+1.10	.4077	+1.34	.2653	+1.4	.2569
+0.8	.0547	.3629	+1.01	.4206	+1.15	.4528	+1.26	.3695	+1.54	.2032	+1.6	.2147
+0.9	.0119	.2144	+1.14	.2422	+1.30	.3027	+1.42	.2863	+1.73	.1316	+1.8	.1490
+1.0	.0000	.0999	+1.26	.0983	+1.44	.1498	+1.58	.1748	+1.92	.0673	+2.0	.0785
+1.1	.0080	.0287	+1.38	.0161	+1.58	.0386	+1.74	.0686	+2.11	.0222	+2.2	.0244
+1.2	.0243	.0009	+1.51	.0029	+1.73	.0000	+1.90	.0061	+2.30	.0015	+2.4	.0007
+1.3	.0392	.0089	+1.64	.0457	+1.87	.0379	+2.06	.0135	+2.50	.0000	+2.6	.0090
+1.4	.0468	.0395	+1.76	.1159	+2.02	.1262	+2.21	.0864	+2.69	.0281	+2.8	.0395
+1.5	.0450	.0776	+1.89	.1807	+2.16	.2198	+2.37	.1913	+2.88	.0656	+3.0	.0776
+1.6	.0358	.1095	+2.02	.2138	+2.30	.2749	+2.53	.2764	+3.07	.1080	+3.2	.1095
+1.7	.0229	.1261	+2.14	.2046	+2.45	.2674	+2.68	.3088	+3.26	.1424	+3.4	.1258
+1.8	.0108	.1239	+2.27	.1592	+2.59	.2030	+2.84	.2467	+3.46	.1538	+3.6	.1215
+1.9	.0027	.1052	+2.40	.0968	+2.74	.1128	+3.00	.1473	+3.65	.1323	+3.8	.0968
+2.0	.0000	.0762	+2.52	.0402	+2.88	.0358	+3.16	.0505	+3.84	.0822	+4.0	.0580

uent S respectively. The problem has been investigated in part by Lord Rayleigh for small values of U and S., *i.e.*, values not exceeding 0.5λ.[1] The aberrations with which we have to deal in the above cases range from 0.03λ for S with the F grating, to

[1] *Phil. Mag.*, (5) **8**, 404.

88λ for U with the W grating. Disregarding the very large values for this latter instrument, we have still to consider the effect of unsymmetrical aberrations amounting to as much as 2.9λ for the J grating. I have therefore extended Rayleigh's results for the effect of an unsymmetrical aberration to values as large as $U=2\lambda$. The values of I_u^2 for $U \cong \frac{1}{4}\lambda, \frac{1}{2}\lambda, \frac{3}{4}\lambda, 1\lambda, 1\frac{3}{4}\lambda$, and 2λ for a rectangular aperture are tabulated in columns 3, 5, 7, 9, 11, and 13, respectively, of Table III. For the sake of comparison the value of I_o^2 for $U=0$ (no aberration), is given in column 2 of the same table. The abscissae a for each curve are expressed as usual in terms of a_o, the angular distance from the center, o, of the geometrical image to the first minimum, m_o, of the normal diffraction pattern I_o^2 (column 2). Owing to the manner in which the integral involved was originally evaluated by Airy,[1] the tabulated values of I_u^2 correspond to different values of a for each value of U.[2]

The curves expressing the relation between I_u^2 and $\frac{a}{a_o}$ for these different values of U (0 to 2λ) are plotted in Fig. 1.

From an examination of the values of the table, or better still, of the above curves, we see that the relation between U, the extreme unsymmetrical wave front aberration, and the angular displacement $o - o'$ of the point of maximum intensity of the resulting distorted image is almost linear, and that the amount of such displacement is

$$o - o' = \Delta\gamma = 0.3\ a_o \frac{\frac{U}{\lambda}}{4}, \tag{2}$$

or, expressed in linear measure at the focal plane,

$$\Delta\xi = 1.2 \frac{u}{b} U . \tag{3}$$

Hence, substituting the value of U from (1), we obtain

$$\Delta\xi = 0.6 \frac{\rho}{\beta} u \sin^3\beta \frac{\sin\theta}{\cos^2\theta}(\cos i + \cos\theta)\cos i , \tag{4}$$

where u is the focal length of the grating.

[1] See *Cambridge Phil. Trans.*, **6**, 402, 1838.

[2] See RAYLEIGH, *Phil. Mag.*, (5) **8**, 405, 406.

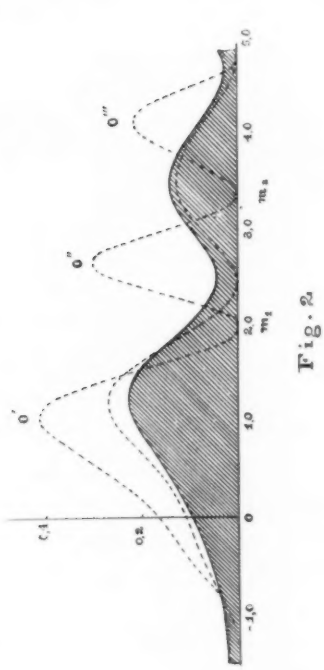


Fig. 2.

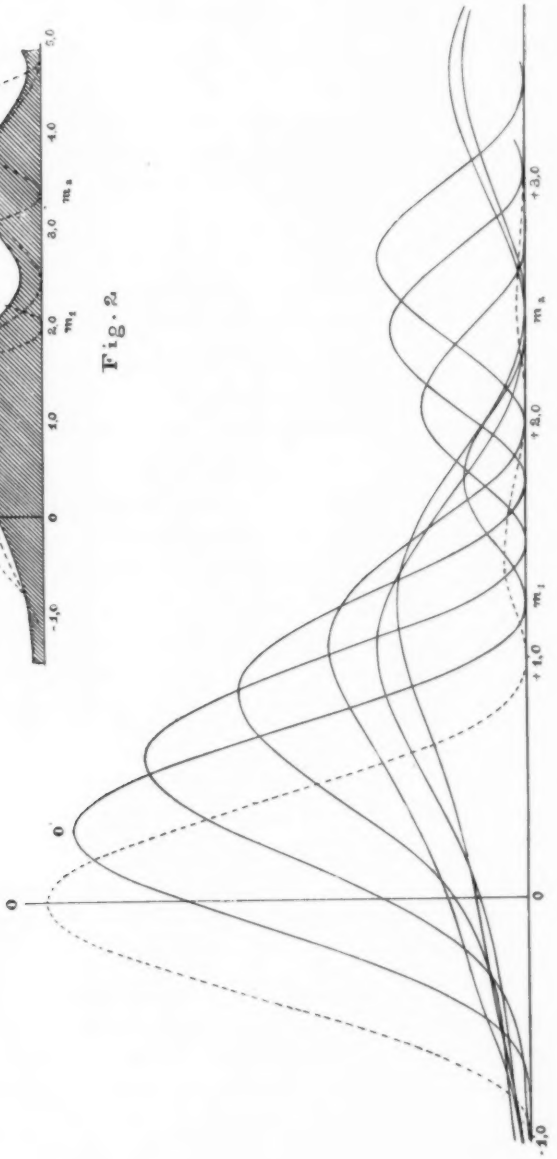


Fig. 1

For the purpose of determining the effect of this displacement on the measurement of wave-lengths it is convenient to express $\Delta\xi$ in terms of $\Delta\lambda$. From the general equation of the grating, we have

$$N\lambda = b(\sin i - \sin\theta) \tag{5}$$

and

$$\begin{aligned} d\lambda &= -\frac{b}{N}\cos\theta\, d\theta \\ &= -\frac{b}{N}\cos\theta\frac{dx}{u} . \end{aligned} \tag{6}$$

If the cross-wires of the measuring micrometer are always set on the point of maximum intensity, o', of the unsymmetrical image, the error in the wave-length measurement due to the aberration of the concave grating spectroscope will therefore be

$$d\lambda = -1.2\frac{U}{N}\cos\theta . \tag{7}$$

These values have been computed for the values of U given by (1) for the four instruments already considered and are found in the columns headed $d\lambda$ of Table II.

The maximum errors of displacement due to aberration are therefore 0.04 tenth-meters in the case of Frost's plates; 0.13 tenth-meters in the plates obtained by Mohler and Daniel; 0.15 tenth-meters in the case of those obtained by Jewell and Humphreys; and so large as to be indeterminate at both the ends and center of the plates obtained by the writer. Comparing these errors of displacement with the quantities ϵ of Table I, which represent the limiting metrological power of the instruments under the best conditions of use, we see that the effect of aberration is to displace the spectral images by amounts which, in the case of gratings F, M, and J, are respectively, about four, fourteen to nineteen, and twenty to one hundred and fifty times as great as the metrological errors of setting on the lines. In the case of grating W, $d\lambda$ is, as already stated, so large as to be indeterminate.

The above considerations are based on the assumption that the setting of the micrometer wire in the measurements for determination of wave-length is affected only by the displace-

ment of the maximum of intensity in the central band of the diffraction pattern. For small values of U this assumption will be very nearly correct, but for large values the setting will also be affected by the depression of the principal maximum, o', and the very decided augmentation of the lateral bands, o'' and o'''. The effect of the symmetrical aberration S will also tend to depress still further the principal maximum, o', and to obliterate the minima, m_1, m_2, m_3, by a re-distribution of the relative intensi ties between the points, m_1o', m_2o'', m_3o''', etc.

In the case of the M and J gratings the extreme values of U are 1.3λ and 2.9λ, respectively. At the same points in the field the corresponding values of S are about 0.1λ. The effect of this amount of symmetrical aberration is to depress the central maximum about 5 per cent. and correspondingly augment the lateral bands. Considering this, and taking into account also the effect of mechanical vibrations, small errors of focusing, etc. all of which tend in the same direction, we shall obtain for these large values of U a distribution in intensity in the spectral image similar to that represented in the shaded curve in Fig. 2. In setting the micrometer wire on such an image as this, the tendency would undoubtedly be to place it considerably farther to the right than the point o', which marks the location of the principal maximum. The error of setting in these cases would therefore considerably exceed the quantity $\Delta\xi$ as given by (3).

In cases like that of the W grating, where the aberration, both symmetrical and unsymmetrical, amounts to a very much larger number of wave-lengths, the central and lateral bands are all blended into a broad indefinite blur on which it is impossible to set the micrometer wire with any pretensions to accuracy. At the points very near the axis of this grating ($\theta = 0$) there is a narrow strip over which the definition is about equal to that at the extreme edges of the field of the M and J gratings; but even here, as we have already seen, the aberrations are from five to twelve times greater than the limit imposed by considerations of "good definition," and from twenty to one hundred and fifty times the limit imposed by the conditions of maximum accuracy. It is for these reasons that the plates taken at Union Springs

have been, as already stated, rejected as unsuitable for accurate measurement.[1]

On account of the small angular and linear apertures of F and J[2] the definition of these gratings is good not only at the center of the plate, but over a fair extent of field. The plates obtained with these instruments have been measured and the wave-lengths of the lines so determined published.[3] Mohler and Daniel have also published a short list of wave-length measurements obtained with grating M.[4]

I have been interested in comparing the apparent accuracy attained in these measurements with that to be expected from the preceding considerations. The probable uncertainties in the wave-length determinations as assigned by the observers themselves are about 0.05 tenth-meters at the center and about 0.2

[1] If the mathematical investigation of the aberration of the concave grating objective spectroscope had been undertaken before, instead of after, these eclipse observations had been made, much disappointment on my own part at least would have been avoided. No excuse can be given for such lack of preliminary examination save that of an unavoidable delay that occurred in organizing and financing the expedition, and the lack of sufficient assistance. The grating had been hastily examined beforehand to test its definition near the axis at the principal focus, and this had been found to be very good. In these tests, however, I had no collimator of sufficiently large aperture to cover the entire surface of the grating, and the semi-angular aperture β was in consequence of this only about six-tenths as large as that used in the actual eclipse work. The aberration on the axis of the grating, was, under these circumstances, only about one-eighth as great as with full aperture, and therefore considerably less than would injuriously affect definition. The effect of increasing the *angular aperture* and the *field* was not considered as carefully as it should have been, but this was partly in consequence of the results which Mitchell had published a short time previously (ASTROPHYSICAL JOURNAL, **10**, 29). As I have already pointed out in my previous paper (*Philosophical Magazine*, July 1903) these results, although obtained with a grating of even larger angular aperture than that here used, should not have been accepted as conclusive. The whole experience is a good illustration of the danger of adopting a new type of instrument without sufficient preliminary examination of its optical defects and limitations in the line of work which it is desired to carry out.

[2] In the case of J the small angular aperture β_2 was due to a part of the ruled surface being defective. In the light of subsequent developments this must be regarded as a rather fortunate accident. Had it not heen for this, the aberration at the edges of the field would have been even larger than it was.

[3] FROST, ASTROPHYSICAL JOURNAL, **12**, 342–344; HUMPHREYS, *ibid.*, **15**, 318–325, Table II.

[4] MOHLER and DANIEL, *ibid.*, **12**, 363.

tenth-meters at the edges of the plates by Frost (pp. 325, 326);[1] and about 1 tenth-meter by Mohler and Daniel (p. 363). In both cases these errors or uncertainties, whichever they may be called, are considerably greater than the theoretical errors of displacement $d\lambda$. At first sight this would indicate that the effect of bad definition due to both the terms U and S is more important than that of the actual displacement $d\lambda$ produced by U alone; and this would probably be the case were it not for the fact that the errors of measurement due to the first cause are likely to be either positive or negative, while those due to the second cause are negative alone. To detect any effect of the latter nature we must examine the residuals, $\lambda_{O.G} - \lambda_R$, for systematic and periodic changes in sign and magnitude. In doing this we are met at the outset with a difficulty which is introduced by the method of reduction and interpolation employed. The values of $\lambda_{O.G}$ from the objective grating plates have been determined not as absolute values, but as relative values, by identifying certain lines on the *O.-G.* plates with lines on the Rowland map, and assuming that the average residuals, $\lambda_{O.G} - \lambda_R$, are zero for these lines and that the spectrum is *normal* between them. This process is a perfectly legitimate and accurate one on plates taken with long focus concave gratings mounted in the manner originally designated by Rowland, and for which there is *no* unsymmetrical aberration. It cannot, however, be adopted without question for the *O.-G.* plates, where conditions both as to curvature of field and aberration are so different.

From equation (5) we have for any point θ in the field of a grating

$$\lambda = \lambda_0 - \frac{b}{N}\sin\theta \ , \qquad (8)$$

where λ_0 is the wave-length of the line which falls on the axis of the grating, $\theta = 0$. When there is an aberrational displacement, $d\lambda$, of the position of the geometrical image, the line of wave-

[1] In this connection it seems desirable to call attention to the fact that Professor Frost himself recognized the inferiority of the wave-length measurements made with the objective grating to those made with the objective prism train, and by far the greater part of his wave-lengths was determined from plates obtained with the latter instrument.

length λ will not fall at the point θ indicated by (8) but at a point

$$\theta_m = \theta + \Delta\gamma \ ,$$

and therefore

$$\theta = \theta_m - 1.2\frac{U}{b} \ , \tag{9}$$

as indicated in (2) and (3). From (1) we obtain for U in terms of θ_m (neglecting powers higher than the fourth) the value

$$U = \frac{\rho}{2}\sin^3\beta\left[a_1 + \left(\frac{5}{6}a_1 - \frac{1}{2}\cos i\right)\theta_m^2\right]\theta_m \ , \tag{10}$$

where

$$a_1 = (1+\cos i)\cos i \ , \tag{11}$$

as defined and tabulated (for different values of i) in my previous paper (Table I).[1]

From (8), (9), and (10) we finally obtain

$$\lambda - \lambda_0 = \Delta\lambda = -\frac{b}{N}\sin\left\{1 - 0.3\sin^2\beta\left[a_1 + \left(\frac{5}{6}a_1 - \frac{1}{2}\cos i\right)\theta_m^2\right]\right\}\theta_m \ . \tag{12}$$

Let us put for convenience

$$\begin{aligned} 0.3\,a_1 &= a_2 \\ 0.3\left(\frac{5}{6}a_1 - \frac{1}{2}\cos i\right) &= a_3 \end{aligned} \ . \tag{14}$$

Then expressing (12) in terms of θ we have to the same degree of approximation as before

$$\Delta\lambda = -\frac{b}{N}\left\{(1 - a_2\sin^2\beta)\,\theta_m - \left[\frac{1}{6} - \sin^2\beta\left(\frac{a_2}{2} - a_3\right)\right]\theta_m^3\right\} \ . \tag{15}$$

The values of a_2 and a_3 which appear in (14) and (15) have, for convenience, been computed for the same values of i used in the table for a and a_1 above referred to. The results are tabulated in Table IV.

TABLE IV.

i	a_1	a_2 $(=0.3\,a_1)$	a_3	i	a_1	a_2 $(=0.3\,a_1)$	a_3
0°	2.000	0.600	0.350	50°	1.056	0.317	0.168
5°	1.988	.596	.348	55°	.902	.271	.139
10°	1.954	.586	.340	60°	.750	.225	.113
15°	1.899	.570	.330	65°	.601	.180	.087
20°	1.823	.547	.315	70°	.459	.138	.064
25°	1.728	.518	.296	75°	.326	.098	.043
30°	1.616	.485	.274	80°	.203	.061	.025
35°	1.490	.447	.249	85°	.095	.029	.011
40°	1.353	.406	.223	90°	.000	.000	.000
45°	1.207	.362	.196				

[1] *Phil. Mag.*, (6) **6**, 130.

When the plate is bent to the focal curve

$$u = \frac{\rho}{1 + \cos i} \cos \theta \tag{17}$$

it has a curvature of $\frac{4}{\rho}$. If it is then straightened and measured on a linear dividing engine we have for the relation between the linear run ΔS of a screw and the angle θ_m

$$\theta_m = \frac{\Delta S}{u_0} = \Delta S \cdot \frac{1 + \cos i}{\rho} . \tag{18}$$

From (8), (15) and (18) we finally obtain

$$\begin{aligned} \Delta\lambda &= -\frac{b}{N}(1 - a_2 \sin^2 \beta)\frac{\Delta S}{u_0} + \left[\frac{1}{6} - \sin^2\beta\left(\frac{a_2}{2} - a_3\right)\right]\frac{N^2}{b^2}(\Delta\lambda)^3 \\ &= A\Delta S + x_c. \end{aligned} \tag{19}$$

If the spectra are both photographed and measured on a flat plate the relation between the run of the micrometer screw and the angle θ_m will be

$$\begin{aligned} \theta_m &= \text{tang}^{-1}\frac{\Delta S}{u_0} \\ &= \frac{\Delta S}{u_0} - \frac{1}{3}\theta_m^3 . \end{aligned}$$

Substituting this value in (15) and reducing as before, we obtain

$$\begin{aligned} \Delta\lambda &= -\frac{b}{N}(1 - a_2 \sin^2 \beta)\frac{\Delta S}{u_0} + \left[\frac{1}{2} - \sin^2\beta\left(\frac{5}{6}a_2 - a_3\right)\right]\frac{N^2}{b^2}(\Delta\lambda)^3 \\ &= A\Delta S + x_f. \end{aligned} \tag{20}$$

The amount from which the spectrum departs from normal is therefore about three times as great when photographed on flat plates as when photographed on curved plates.

In the case of Frost's measurements, in which the plates used were flat, the extreme value of $\Delta\lambda$ (see Table I) was about 400 tenth-meters. The value of $\frac{N}{b} = n$ for the F grating is 5684×10^{-8}. Hence the value of x_f, the second term of (20), which expresses the correction required to a "normal" spectrum is about

0.1 tenth-meter.

The corrections at the intermediate points, $\Delta\lambda = 100$, 200 and 300 tenth-meters, are respectively

For $\Delta\lambda = 100$ tenth-meters, $x = 0.002$
For $\Delta\lambda = 200$ tenth-meters, $x = 0.013$
For $\Delta\lambda = 300$ tenth-meters, $x = 0.043$
For $\Delta\lambda = 400$ tenth-meters, $x = 0.103$.

Plotting these values as abscissae and ordinates respectively we obtain the curve in Fig. 3. This expresses graphically the corrections that must be applied to the measurements on the assumption that the spectrum is normal over the entire field.

In the actual reduction of the plate the necessary corrections were somewhat reduced by dividing the plate into three sections; the first extending from λ4200 to 4383, the second extending from λ4383 to 4572, and the third from λ4572 to 4950. The spectrum was assumed normal over each of these three sections. As the constant A of the micrometer screw was determined separately for each section, the corrections between these points would be the differences between the ordinates to the curve, *a*, *b*, *c*, *o*, *d*, *e*, and the straight lines, *ab*, *bc*, and *cd*. The maximum correction in section I (*ab*) would therefore be about 0.015 tenth-meters, in section II (*bc*) not more than 0.004 tenth-meters, and in section III (*cd*) about 0.03 tenth-meters.

In section I the correction is just a little larger than the limit of metrological power ϵ (see Table I), and in section II it may be entirely disregarded; in section III, however, it is about three times as large as ϵ. In this last section the correction is sufficiently large to make its neglect felt in the sign of the residual errors. In order to determine whether this were true I formed a table of residuals, $f(\lambda) =$ Rowland − Frost, for all lines whose identification was assumed to be reasonably certain. These residuals are plotted in Fig. 4 and the sums taken for each interval of 100 tenth-meters (from 4200 to 4300, from 4300 to 4400, etc.). The latter quantities are indicated by the circled crosses ⊗ of the figure.

These averaged residual differences correspond in distribution and sign to those which would be produced by neglect of the correction x for sections I and II, but are larger in magnitude than would be expected. For section III they also correspond if the constant of the micrometer run was determined by settings

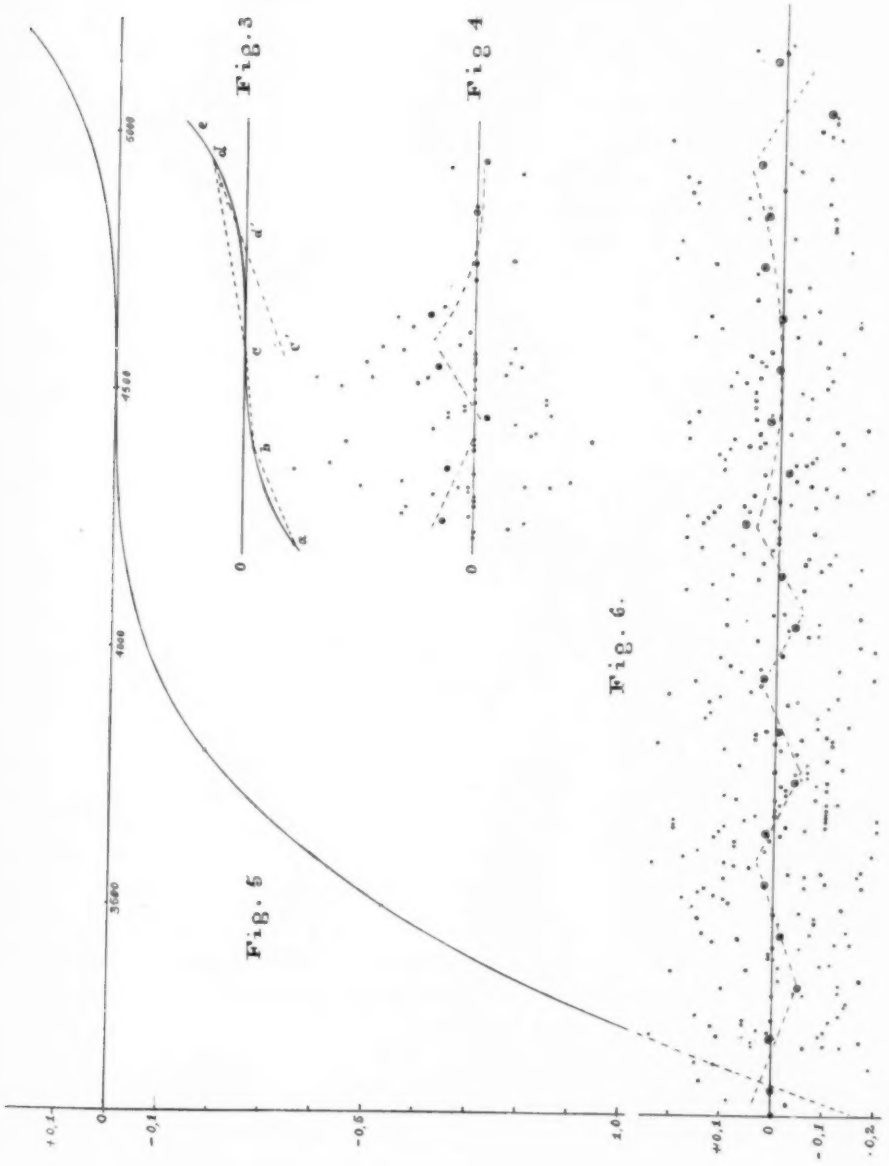


Fig. 3
Fig. 4
Fig. 5
Fig. 6
a
b
c
d
e
0
5000
4500
4000
3500
+0,1
-0,1
-0,5
1,0
-0,2

on lines near d and d', or was assumed to be the same as in section I. In such case the line dc would be parallel or nearly so to the line ab as at dc', and the corrections for x would be the differences of the ordinates to dc', and the curve c, o, d, e. These are nearly the same, not only in sign but also in magnitude, as those actually found. The processes employed in the work of reduction of the plates are not stated in sufficient detail by Professor Frost to enable us to determine whether or not this explanation is the correct one, but the periodic character of the averaged residuals, $\Sigma f(\lambda)$, is quite striking and the great preponderance of residuals of positive sign is an evidence of some systematic error of the kind indicated.

In the case of Humphreys' measurements the plates were curved. The maximum values of $\Delta\lambda$ (see Table I) measured are

$$+\Delta\lambda = 700$$
$$-\Delta\lambda = 1400 .$$

The values of x_c (from 19) are

For $\Delta\lambda =$ 200 tenth-meters, $x_c = 0.004$
For $\Delta\lambda =$ 400 tenth-meters, $x_c = 0.034$
For $\Delta\lambda =$ 600 tenth-meters, $x_c = 0.117$
For $\Delta\lambda =$ 700 tenth-meters, $x_c = 0.185$
For $\Delta\lambda =$ 800 tenth-meters, $x_c = 0.276$
For $\Delta\lambda =$ 900 tenth-meters, $x_c = 0.394$
For $\Delta\lambda =$ 1000 tenth-meters, $x_c = 0.538$
For $\Delta\lambda =$ 1100 tenth-meters, $x_c = 0.716$
For $\Delta\lambda =$ 1200 tenth-meters, $x_c = 0.930$
For $\Delta\lambda =$ 1300 tenth-meters, $x_c = 1.182$
For $\Delta\lambda =$ 1400 tenth-meters, $x_c = 1.476$

In this case the correction required for curvature at the violet end of the spectrum is nearly five hundred times the limiting metrological power, ϵ.

The relation between $\Delta\lambda$ and x is plotted in Fig. 5. The residuals $h(\lambda) =$ Rowland $-$ Humphreys, and their sums over each interval of 100 tenth-meters, have been found in the same way as for Frost's measurements and are plotted on the same scale in Fig. 6.

In this case also there is a marked correspondence between x and the residuals $\sum_{0}^{100} h(\lambda)$. Near the center of the plate where the spectrum is nearly normal and x is small, the average residuals, $\Sigma h(\lambda)$, are also small and lie very nearly in a straight line parallel to the λ axis. As we go from this point toward the violet the residuals become distinctly periodic in character. This would be explained if the wave-lengths in this part of the spectrum were determined by extrapolation from standard reference lines at about 3250, 3500, 3700, 3850, 4000 and 4150. In Humphreys' paper the method of reduction is not described, and here again it is not possible to satisfactorily compare the actual results of computation and measurement.

EFFECT OF ABERRATION ON THE APPEARANCE OF THE LINES.

For small values of θ, *i. e.*, near the center of the plate, the value of U is small and the value of S is relatively large. In this portion of the field the lines will therefore be simply broadened without being sensibly displaced or rendered assymmetrical. As we go away from the center the value of S decreases and the value of U increases. The effect of this is not only to displace the apparent center of intensity of the central image but to increase very greatly the relative intensities of the lateral diffraction fringes on the right hand, *i. e.*, the violet side, of the central image.

An examination of Fig. 2 shows that for large values of U the first lateral fringe on the right becomes very nearly as bright as the central image, and is much narrower and sharper. This image was actually selected by Humphreys as the one corresponding most nearly to the true geometrical image. The multiplication of lateral images at the edges of the field is not, as Humphreys assumes, an evidence of imperfect focusing, but of *good* focusing. Under favorable conditions it is possible to observe not only the principal (central) component of the diffraction image and the first two right hand fringes (forming an apparent tripling of the line) but several more lateral fringes still further to the right.

ALLEGHENY OBSERVATORY,
March 1903.

THE FLUORESCENCE AND ABSORPTION SPECTRA OF SODIUM VAPOR.

By R. W. Wood and J. H. Moore.

THE FLUORESCENCE OF SODIUM VAPOR.

The green fluorescence which sodium vapor exhibits when illuminated with an intense beam of white light, was first observed and studied by Wiedemann and Schmidt.[1] The method which they employed was to heat the metal in an exhausted glass bulb, concentrating a beam of sunlight on the vapor by means of a lens. A cone of green light is seen where the intense beam enters the mass of metallic vapor. Examined with the spectroscope, this light was found to consist of a band in the red, a narrower band nearly in the position of the D lines, and a broad green band which appeared to be broken up into channels or bands. The wave-lengths of some of these bands were roughly determined, but the authors do not appear to have determined exactly the relation which they bore to the absorption bands which appear in the same part of the spectrum.

Inasmuch as we have at the present time no very satisfactory theory of fluorescence, and as practically all quantitative work has been done with solutions, it seemed worth while to make a careful study of the relation between the fluorescent light emitted by sodium vapor and the light absorbed by the vapor under the same conditions. The chief points of interest which have been brought out by these investigations are the establishment of the fact that the fluorescent spectrum coincides exactly with the absorption spectrum, band for band and line for line, and a determination of the relation existing between the wave-length of the light which provokes the fluorescence and the nature of the fluorescent spectrum. The somewhat remarkable fact has been ascertained that the D line absorption

[1] *Wied. Ann.*, 57, 447, 1896.

is in no way connected with the production of the fluorescence, though the absorption at this point of the spectrum is much more intense than at any other.

By means of improved apparatus we have not only been able to photograph the fluorescent spectrum by means of a concave grating, but have been able to observe by means of a grating the fluorescent spectrum when provoked by approximately monochromatic light obtained with the Fuess monochromatic illuminator. The results of the work throw a great deal of light on the mechanics of the sodium molecule, and will doubtles prove of considerable value in the development of the theory of fluorescence.

APPARATUS EMPLOYED.

The fluorescence as observed in exhausted glass bulbs is never very intense, and the experiments can be continued only for a few moments owing to the speedy corrosion of the glass surface. Moreover, it is not possible to make use of very dense vapor, the generation of which requires a high temperature, owing to its action on glass. The form of tube which was employed by one of us in a previous investigation on the subject[1] enables vapor of great density to be obtained, but owing to the rapid distillation to colder parts of the tube, the experiment cannot be continued long enough for satisfactory photographic records. It is important not only to have a very dense vapor, but also to have the vapor confined within a small region and sharply bounded, in order that the light may not be weakened by absorption before it reaches the denser portions. To meet these requirements a new form of tube was designed and constructed which gave admirable results. With it a fluorescence ten or fifteen times as bright as anything that can be secured with glass bulbs was obtained and maintained continuously for five or six hours without recharging the tube. This tube we have had in action for fully forty hours, and it is only just beginning to show signs of leakage around the brazed joints, due to the action of sodium at a red heat on the silver, with which the joints were brazed. The tube can be very easily constructed, and when

[1] R. W. Wood, *Proc. R. S.*, **69**, 157; also *Phil. Mag.*, (6) **3**, 141, 1902.

once charged can be used over and over again without any preparation whatever, for the exhibition of this most beautiful example of fluorescence. Its general form is shown in Plate II, Fig. 1. The large tube was a piece of three-inch (sixteen gauge) Shelby seamless steel tubing, two feet in length. A ten-inch piece of thin three-fourths inch steel tubing was brazed with silver into the large tube at the center, making a right angle with it. (Fig. 2, is a cross section of tube.)

Immediately below this tube, and at a right angles to both, a small iron crucible was brazed into the larger tube, projecting into its interior to such a distance that its rim was visible through the side tube. This crucible was made by boring out a three-fourths-inch iron cylinder. A small piece of brass tubing was also brazed into the large tube near one end, through which the whole could be exhausted. The crucible was filled with lumps of sodium, and the ends of the large tube closed with plate glass, carefully cemented on with sealing wax. The side tube was then closed in the same manner, and the whole exhausted to a pressure of about a millimeter, by means of a mercurial pump. The tube was then sealed off from the pump, a small piece of glass tubing having been cemented into the brass tube and drawn down into a capillary.

The tube was now mounted in a horizontal position and a large Bunsen burner placed beneath the crucible, which was soon raised to a red heat. The dense sodium vapor poured out of the mouth of the crucible and gradually condensed on the cooler portions of the tube. Sunlight from a heliostat was sent down the large tube, a lens placed close to the glass window forming an image of the Sun immediately above the neck of the crucible. On looking down the side tube an intensely brilliant green cone of light was seen, many times brighter than anything that has ever been obtained with glass bulbs. The floating specks of oxide which appear when the tube is first heated, and which shine with a dazzling white light, soon disappear and leave the fluorescence entirely uncontaminated. It is apparent that with this arrangement light enters at once into the densest vapor without suffering previous loss by absorption in vapor of less density.

PLATE II.

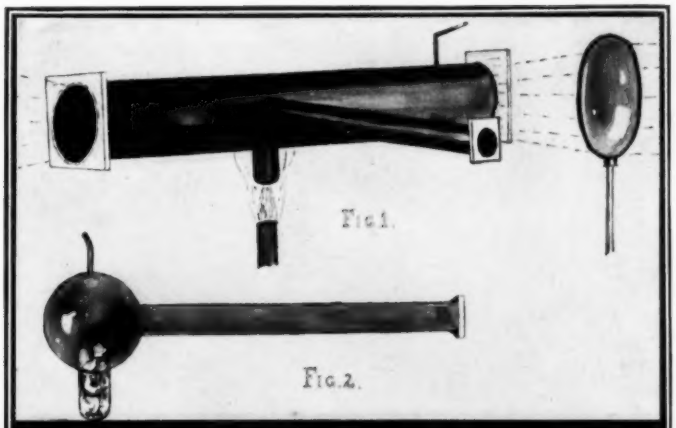


Fig. 1.

Fig. 2.

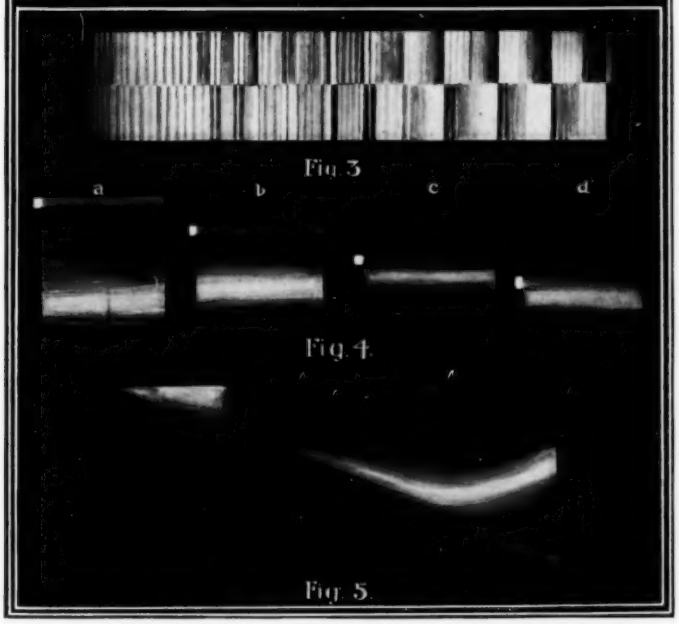


Fig. 3

Fig. 4

Fig. 5.

Red
Yellow
D_1 D_2

Green blue

Blue

Red
Orange
Yellow
Green
Gr.-Blue
Blue

Moreover, the fluorescent light passes down the observation tube without having to traverse more than a very thin layer of the vapor, a matter of considerable importance, as we wish to examine the fluorescent light unmodified by subsequent absorption. The large amount of sodium which could be stored in the crucible enables us to deliver a dense stream of vapor in front of the observation tube for a very long time, which is absolutely essential if photographic records are to be obtained.

SPECTRUM OF THE FLUORESCENT LIGHT.

The spectrum of the fluorescent light was first examined with a two-prism Steinheil spectroscope. The spectrum consisted of a red band and a green band, the latter appearing distinctly fluted. No trace of any bright line or band at or near the position of the D lines has ever been seen in any of our experiments. Its presence in the spectrum described by Wiedemann and Schmidt, and also by one of us, may possible have been due to the fact that in both of these cases the vapor was contained in a glass bulb heated by a Bunsen burner. This flame, colored by the sodium of the glass, may have been responsible for the appearance of a bright line in the place mentioned, a matter which can be very easily settled by repeating the experiments with the bulbs.

The marked resemblance which the fluted spectrum bears to the absorption at once suggests that it may be due to the fact that the fluorescent light has to pass through a certain amount of vapor before reaching the spectroscope; in other words, that it does not belong to the fluorescent spectrum at all, but is the result of absorption. To determine whether or not this was the case, an absorption comparison spectrum was formed by throwing some of the light which had passed through the tube into the instrument by means of a couple of mirrors and a small right-angled prism. It was at once apparent that the bright lines and bands of the fluorescent spectrum were exactly out of step with those of the absorption spectrum. To secure a fixed record of this fact, a camera was attached to the spectroscope and the two spectra photographed. The spectrogram confirmed the

visual observations in every respect, but the dispersion was too small to make the pictures very satisfactory.

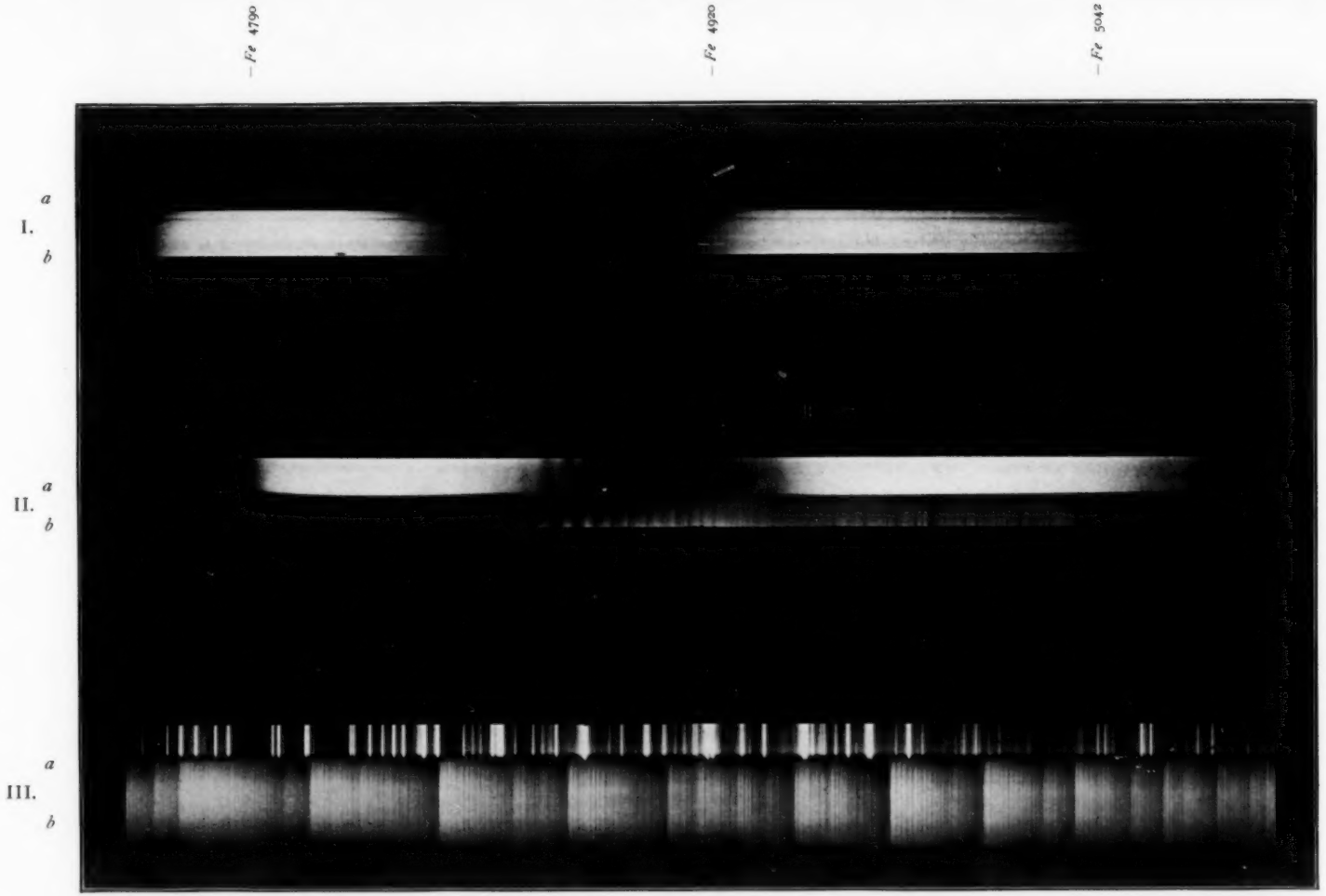
A Rowland concave grating with 15,000 lines to the inch, of one meter radius, was then used in place of the spectroscope, and some excellent photographs were obtained with an exposure of less than an hour. The fluorescent spectrum was found to extend from wave-length 5340 to wave-length 4600 in the green and blue region. All of the photographs show in addition a faint solar spectrum extending from the end of the fluorescent spectrum down to the H and K lines. This is due to a small amount of white light which is scattered by occasional specks of oxide, or perhaps reflected from the wall of the tube. So far as we have been able to determine, the fluorescent spectrum is not contaminated with solar lines, since it is located in a less actinic region, and the scattered light is not of sufficient intensity to leave any appreciable record in this region.

These photographs brought out the remarkable fact that the fluorescent spectrum is the exact complement of the absorption spectrum. The two spectra were photographed in contact on the same film, and either one might have been a contact print taken from the other. In the upper spectrum, for example, there were two broad light bands with a fine dark line down the center, while in the lower spectrum occurred two broad dark bands with bright lines down the center. This same thing was true for all of the irregularities of shading in the very complicated fluted spectrum. A number of these photographs are reproduced in Plate III, Figs. 2 and 3. As most of the fine detail will doubtless be lost in the process of reproduction, a very careful drawing of the two spectra has been prepared from the original negative, which is reproduced with the direct records. (Plate II, Fig. 3. Absorption spectrum above, fluorescent spectrum below.)

The fluorescent spectrum in the green-blue region may be divided into three groups of bands: (1) those from λ 5340 to λ 5080, consisting of six broad hazy bands, which correspond in position to the fluted bands of the absorption spectrum; higher dispersion would doubtless resolve them into lines; (2) those

PLATE III.

PLATE III.



I (*a*). Absorption spectrum of sodium vapor. (Region from λ 4750 to λ 5100.)
(*b*). Corresponding comparison spectrum of iron.
II (*a*). Fluorescent spectrum. (The solar spectrum showing at the left half of the plate is due to diffuse light.)
(*b*). Absorption spectrum, taken with same grating.
III (*a*). Absorption spectrum, (*b*) fluorescent spectrum, showing their complementary character.

from λ 5080 to λ 4865, a group of irregularly fluted bands, the heads of which point toward the red; *i. e.*, they are strongest on the less refrangible side and shade off on the side of the shorter wave-lengths; (3) those from λ 4865 to λ 4600 which appear, under the dispersion used, as uniform narrow bands. The spectrum is the exact complement of the absorption spectrum taken with the same instrument, and further work with the concave grating of fourteen feet radius will show whether all of the very minute and narrow lines in the flutings of the latter spectrum are present in the former. We feel sure that the spectrum can be photographed with the large grating without difficulty.

Visual observations have shown that the red fluorescence is also fluted, though the flutings are only to be seen when the vapor is very dense and the illumination very intense. It has not yet been definitely proven whether this fluting belongs properly to the fluorescent spectrum or is the result of absorption. A new form of tube has been designed which, it is believed, will give a much denser vapor and make the settlement of this question possible.

The complementary nature of the photographs of the fluorescent and absorption spectra might lead one to suppose that the wave-length absorbed was re-emitted without change of wave-length. To test whether or not this was the case, it was necessary to illuminate the vapor with monochromatic light.

The Fuess monochromatic illuminator, which enables one to cut out a region of any width from a very intense solar spectrum and focus this light at a definite point in space, was arranged so as to send a cone of violet light down the tube, the rays meeting just above the mouth of the crucible. No fluorescence was detected. On gradually increasing the wave-length of the light, by turning the graduated screw which rotated the prisms of the instrument, it was found that the fluorescence appeared when wave-length 4600 was reached. On looking into the end of the large tube a very beautiful phenomenon was seen. The cone of deep-blue monochromatic light was distinctly visible, owing to

traces of oxide floating about, while at the point where the rays met in the dense sodium vapor there appeared a brilliant spot of *green* fluorescent light. As the wave-length was further increased, this spot increased in brilliancy, still remaining green, passed through a maximum, and then gradually faded away, disappearing entirely when the illuminating light became yellow. The vapor remained dark until the wave-length of the light exceeded that of the D lines, when the red fluorescence gradually developed, passing through a maximum in the same manner and then fading away.

The fluorescence of the vapor produced in this way was much less brilliant than in the former experiment, since the total radiant energy thrown into the vapor was very much less than when direct sunlight was employed; still the light sent down the lateral tube was intense enough to give a spectrum when the Steinheil spectroscope was directed down the tube. This spectrum was very feeble, however, and it was only with great difficulty that the changes could be followed which took place when the wave-length of the illuminating beam was changed. When blue light was employed, the complete green fluorescent spectrum seemed to be present with a maximum intensity at the yellow end. As the wave-length of the light was increased, the point of maximum intensity in the fluorescent spectrum moved toward the blue.

The important bearing which the phenomenon has on the theory of fluorescence made a more careful study of the relation between the wave-lengths of the absorbed and emitted light very desirable. To accomplish this, the arrangement of the apparatus was changed in the following manner: the monochromatic illuminator was rotated through a right angle, so that its emitting slit was horizontal, instead of vertical. The dense sodium vapor above the mouth of the crucible was now illuminated with a thin horizontal sheet of monochromatic light (the image of the horizontal slit of the illuminator projected in space by a lens). This arrangement, of course, limits the fluorescence to a thin horizontal layer of vapor, which, when viewed through the lateral tube, appears as a narrow line of bright green light. By viewing the

sheet of vapor edgewise we get a much more intense light, and since its width is small, we can dispense with a spectroscope entirely, simply viewing it through a prism or grating.

A small transmission grating of 14,480 lines to the inch, which gives a first-order spectrum nearly as bright as a 60° flint prism, was mounted in front of the lateral tube, and the line of fluores cent light viewed through it, the head being covered with a black cloth to cut out all extraneous light. It was found that by slightly inclining the large tube to the illuminating beam, it was possible to illuminate a minute projection on the inside edge of the lateral tube with the monochromatic light which caused the fluorescence; in other words, the near end of the horizontal image of the slit was brought upon this projection. The line of fluorescent light was thus tipped at one end with a small point of light similar to the light which produced the fluorescence. The spectrum of this small illuminated spot, which was of course a narrow band, fell alongside of the fluorescent spectrum, enabling a comparison to be made at once. Any exception to Stokes's law would make itself evident as an extension of the fluorescent spectrum on the more refrangible side of the position occupied by the small spot of illuminating light.

Some very remarkable and significant results were obtained with this disposition of the apparatus. Starting with violet illu-mination, there appeared through the grating only the small comparison spot of light which moved along as the wave-length was increased. As soon as wave-length 4600 was reached, the fluorescent spectrum appeared. Its appearance is indicated in Plate II, Fig. 4*a*. A strip of blue fluoresent light continuous with the reference spot showed that light of the same wave-length as the absorbed light was being emitted by the vapor. A region of darkness occurred on the less refrangible side (usual sense of the term), and then came a broad green band with a maximum of intensity on the end toward the yellow. Then came another gap extending considerably above the D lines, followed by a *very faint* trace of the red fluorescent band (not shown). On gradually increasing the wave-length of the light the following changes were noted. The spot of reference light, accompanied

by its fluorescent prolongation, moved up the spectrum, pushing the dark region before it, while the point of maximum fluorescence in the wide green band moved down the spectrum to meet the advancing spot. These changes are represented in Fig. 4 *b*, *c*, *d*, the point of maximum fluorescence nearly coinciding in position with the reference spot in *d*. On still further increasing the wave-length, the fluorescence became very faint, and appeared to extend a little farther down the spectrum than the position occupied by the small spot of light. This means an exception to Stokes's law when the wave-length of the illuminating light (green) has the maximum value which still yields fluorescence.

In Plate II, Fig. 5, an attempt has been made to represent these changes in the conventional way.[1] Everything shown in this diagram is, however, due to fluorescence, the deviated continuous spectrum of the light exciting fluorescence having been omitted. It will be seen that there is an emission of fluorescent light of the same wave-length as that of the exciting light, which gives the diagram an appearance not unlike the diagrams where the deviated continuous spectrum is shown. To make this diagram exhibit the changes just described, one has only to move a narrow vertical slit across it from right to left.

It was impossible to tell whether flutings were present in any portion of the fluorescent spectrum or not, owing to the comparatively wide source, and small dispersion employed. There is no reason for believing that they are not, but it does not seem safe to assume that the spectra are identical when the fluorescence is produced by white light and monochromatic blue light. The extent of the spectrum, and the distribution of the intensity in it, have been shown to be different in the two cases, and the flutings, say in the green, which are present when white light is used, may be absent when the fluorescence is produced by light of much shorter wave-length. To test this the spectrum will have to be photographed when the tube is illuminated with monochromatic blue light. To accomplish this with the present apparatus would probably require an exposure of six or eight

[1] MÜLLER-POUILLET, *Lehrbuch der Physik*, II, 1, 368.

hours. More favorable conditions are expected with a new form of tube now under construction, and it seems probable that we shall eventually learn a good deal about the dynamics of the sodium molecule. The results already obtained apparently prove that the light of longer wave-length emitted when the vapor is fluorescing is not the result of damping of the vibration, as assumed in Lommel's theory, but an emission resulting from the fact that the ions of longer free period are set in vibration either by the waves of shorter period or by the ions of short period which are thrown into vibration by these waves. It is not worth while to speculate about this, however, until the fluorescent spectrum produced by monochromatic blue light has been photographed.

In general, the fluorescence of a substance has its maximum intensity when the wave-length of the light is that of the light most strongly absorbed. Sodium vapor is an exception to this rule, for the D line absorption, which is far more intense than the fluted absorption, has nothing to do with the fluorescence. On Lommel's theory of fluorescence, the absence of any lateral emission of light by an absorbing medium is explained in one of two ways: either the absorption is of waves of different period (an octave below, for example) from the free period of the ions, or else the damping factor is so large that the emitted light lies in the infra-red region. In the case of sodium vapor, neither explanation is sufficient to account for the absence of fluorescence when the wave-length of the exciting light is that of the D lines, for, since Kirchhoff's law is obeyed in this case, the absorbed waves and emitted waves have the same period, and the absorption is a resonance phenomenon; moreover, the damping factor must be very small, since we have interference with large path-difference in the case of sodium light. The non-luminous vapor employed in these experiments may, of course, be in a different state from the vapor in a sodium flame, but even if this be the case, it does not seem justifiable to assume a large amount of damping, for this should cause a displacement of the absorption lines with reference to the position which they occupy in the case of absorption by a sodium flame.

It is worthy of note that lines corresponding in position to the fluted bands are absent in the emission spectrum of sodium vapor, except perhaps in the case of the temperature emission studied by Evershed, which does not appear to have been studied under high dispersion.

There seems to be no way of explaining the emission of the green light when the vapor is illuminated with blue light. It cannot be the result of the damping of the ions, whose free period is that of the blue light, for it is in all probability a discontinuous spectrum complementary to the fluted absorption spectrum.

It will be interesting to see whether the absorption of the vapor is directly affected by the circumstance that it is fluorescing at the same time. This was found to be the case in some experiments made by Burke upon uranium glass. It is also important to determine in what way the absorption and fluorescence are influenced by pressure. These matters will be investigated in the near future.

The statement that, when the wave-length of the exciting light is that of the D lines, no fluorescence is produced, requires modification. Strictly speaking, this is not true, though it is almost certain that the D line absorption is in no way responsible. This is due to the fact that the beam from the monochromatic illuminator is not strictly monochromatic, being in fact a band varying from ten to twenty Ångström units in width. As we shall show in the part of this paper dealing with the fluted absorption of the vapor, the fine lines can be traced up to the very edges of the broad band produced by the widening of the D lines when the vapor is very dense. It is unquestionably the absorption at these lines which gives rise to the very feeble reddish fluorescence which can be seen when the light furnished by the monchromatic illuminator is symmetrical about the D lines. Strictly monochromatic light of the wave-lengths of D_1 and D_2, no matter how intense, we feel sure would produce no fluorescence, unless the flutings actually cross this region, which is very likely the case. The only light which produces no fluorescence is green light in the vicinity of $\lambda 5530$ and the violet

below λ 4600, which, as we have shown, is all that is transmitted by the vapor when it is very dense.

THE ABSORPTION SPECTRUM OF SODIUM VAPOR.

The fluted absorption spectrum of sodium vapor was first observed and studied by Roscoe and Schuster in 1874. Subsequent investigations were made by Liveing and Dewar in connection with their work on the reversal of the lines of metallic vapors, and also by one of the writers.

Previous experiments by one of us having shown that it was impossible to secure photographs of the fluted spectrum with the concave grating, using the arc as a source of light, that were not contaminated by bright lines from the vapor of the lamp, it was necessary to find a source of light of great intensity and having a continuous spectrum. After experimenting with various sources of light, we finally adopted the Nernst lamp, which was found to fulfil the conditions specified.

In the first series of experiments the sodium was vaporized in an atmosphere of hydrogen, generated by electrolysis, and dried by passage over calcium chloride and phosphorus pentoxide. In order to remove traces of oxygen which caused the tube to smoke, the gas was finally passed over red-hot copper gauze. The metal was heated in tubes of thin steel, the ends of which were closed with plate glass. In the later experiments the tubes were exhausted with a mercury pump, and the metal volatilized in a vacuum. The latter method was found to be most satisfactory. The spectra were found to be identical in the two cases.

The tubes were either heated by means of Bunsen burners, or by a coil of No. 20 iron wire, insulated from the tube by a thin layer of asbestos board. The vapor is more uniform when the tube is heated electrically, for if the upper side of the tube is colder than the lower, a non-homogeneous medium results, the density being greatest along the floor of the tube. A Bunsen burner is better, however, for some experiments, where a very dense vapor is required. With it the metal does not distil so rapidly to the colder parts of the tube, and, with careful reg-

ulation of the flow of gas to the burner, it was used very successfully in many of the experiments.

The absorption spectrum was photographed with a fourteen-foot concave grating in the first order, the time of exposure varying from twenty minutes to an hour, according to the density of the vapor. The second-order spectrum was observed from time to time during the exposure, in order to keep the density of the vapor properly regulated.

It was found that the best results were obtained with a slit-width of 0.065 mm. The width of the slit for the iron comparison spectrum was 0.030 mm. In order to eliminate any errors due to changing the width of the slit, photographs were taken of both spectra with a slit-width of 0.030 mm, and the measurements made with the two sets of plates compared. The plates were measured on the dividing engine of the laboratory, and the measurements can be considered accurate to within 0.05 of an Ångström unit. The ultra-violet region was explored in the same manner, using a tube closed with quartz plates. No traces of any flutings were found, but the lines of the principal series were strongly reversed.

The fluted absorption spectrum makes its first appearance when the D lines are two or three Ångström units in width. It begins as nine bands, the heads of which point toward the violet end of the spectrum, *i. e.*, in each band the absorption decreases from the head toward the longer wave-lengths. The heads of the bands as they first appear are:

I.	4783.35	VI.	4932.97
II.	4809.92	VII.	4962.96
III.	4837.72	VIII.	5001.94
IV.	4865.60	IX.	5040.71
V.	4894.94		

There is also evidence of absorption lines in the first seven bands. These lines, however, do not come out strong at this stage, but appear as a slight shading on the bright background. In Band I can be seen the line λ4793.10; in Band II, line λ4820.72; in Band IX, λ5053.50, and in Band VII, λ4979.28, which appear as fainter heads of small bands into which the

others break up. Bands V and VI are about the center of the region of absorption.

A very slight increase in the density of the vapor is sufficient to bring out the heads of the bands as strong dark lines, as well as the fainter heads in the bands themselves. The bands are now seen to be made up of an immense number of lines, some of which are broad and some exceedingly fine, and in some of the bands there is an appearance as if two series were superposed.

At this time the region of absorption extends from about λ4600 to λ5200, a series of three bands, the more refrangible edges of which are broken up into smaller bands, appearing between λ5079 and λ5200, and a series of twelve bands, each of which is divided into smaller bands coming into view between λ4780 and λ4600. The wave-lengths of the principal lines in the fluted spectrum have been carefully measured by comparing them with standard lines in the iron spectrum.

A fluted absorption spectrum makes its appearance in the red and orange portion, when the density of the vapor is such as to give the green-blue flutings at their best. This spectrum has not been photographed and measured at the present, owing to the difficulty of getting plates sufficiently sensitive to the red. The Erythro plates, which were used by one of us in securing photographs of this region with a fourteen-foot grating some years ago, are no longer on the market, and the few experiments which we have made in sensitizing our own plates have been only partially successful. This region will be studied as soon as suitable plates can be obtained.

As the density of the vapor is further increased, the greenish-blue region disappears entirely, and the fine lines can be traced nearly up to wave-length 5400 from the blue end of the spectrum, and from the red end they are seen to fill the spectrum quite up to the broad D line absorption, which is now forty Ångström units in width. On crossing this broad black band the fine lines make their appearance again, which makes it seem probable that the red fluted spectrum crosses the region occupied by the D lines. A further increase in the density results in blotting

out the red, orange, and yellow completely, leaving only a rather narrow green region, the center of which is at wave-length 5530, and the violet below λ4600. The color of the transmitted light is now a very deep violet. The fine lines can be pushed into the green band from its opposite edges, and traces of them have been found all through it. Finally a very black broad band appears at the center of the green strip, which in a spectroscope of small dispersion appears as a rather narrow line. The center of this band is at wave-length 5530, approximately. We have not been able to photograph it with the grating, owing to the feebleness of the light, and the difficulty of keeping the vapor at this great density for a sufficient length of time; but its position was determined visually with a grating of about eight feet radius. This band has been seen by previous observers (Liveing and Dewar) and is described as persisting until the last traces of the fluted spectrum disappeared, as the vapor cooled off. We cannot understand this, for we have found it only when the vapor had the maximum density attainable, namely, when the blast-lamp played directly against the bottom of the tube, raising it to a bright red heat.

In order to see if an increase in the length of the absorbing column of the vapor produced the same effect as increasing the density of a short column, a steel tube five feet in length was used. In this were placed eight lumps of sodium of the same size, at intervals of about six inches. Eight Bunsen burners were regulated so that when one of them was placed under a lump of sodium the D lines were strongly reversed, but no trace of the fluted spectrum appeared. On adding burner after burner, exactly the same sequence of events were observed as in the previous experiments, where the density of the vapor was increased by raising the temperature of the tube. Though this was to be expected, it seemed worth while to try the experiment.

We have measured the wave-lengths of about 460 of the strongest lines between wave-lengths 4616 and 5738, which are given in the following tables :

WAVE-LENGTHS OF THE PRINCIPAL LINES AND BANDS IN THE ABSORPTION SPECTRUM.

GROUP A. λ 4600–5200.

Wave-Length	Character	Wave-Length	Character	Wave-Length	Character	Wave-Length	Character
4616.42	f	4815.84	8 b	4858.05	7 fine	4889.84	8
52.04	f	16.49	6 fine	58.75	8	90.75	7
52.18	b.h.	17.14	7 fine	59.67	7	91.52	9
59.60	b.h.	17.64	8 fine	60.41	8	92.43	7 fine
84.69	fine	18.57	8 b	60.99	fine	93.28	10 b
92.89	7	19.64	8	61.52	fine	94.13	6 fine
4704.36	1	20.72	7	61.78	fine	95.00	H 0.7
07.09	7	21.88	8	62.21	9		wide
09.72	1	23.15	7 fine	63.02	fine	96.06	4
18.29	7	23.82	8	63.78	6 b.h.	97.02	8
21.33	8	24.46	8 fine	64.45	fine	97.92	6
24.42	8	25.81	7 fine	64.88	7 fine	98.96	7 b.h.
28.82	8	26.58	8 fine	65.67	H broad	99.99	6
32.77	6	27.27	7 fine		0.4 wide	4900.94	9
35.78	6 b	27.99	8 fine	66.64	7	01.86	8
36.67	8	28.66	9 fine	67.44	7	02.64	4 fine
40.95	8 fine	30.28	8 b.h.	68.53	7	04.96	6
47.56	8 fine	32.83	8	69.54	8	05.79	7 fine
58.55	7 b.h.	33.47	9 b	70.01	10 b.h. Hs	06.43	4
51.96	8.5	35.36	fine	70.44	7 fine	07.16	7 b.h.
53.83	8.5	36.10	fine	71.33	8 b	08.22	9
58.68	9	36.51	7	72.05	fine	08.84	fine
60.85	7 fine	36.93	7	72.59	fine	09.47	9
61.86	7 fine	37.71	H *broad head* 0.5 wide	73.01	fine	10.12	fine
63.05	8 fine			73.50	fine	10.73	8
64.98	9 b	38.92	9 b.h.	73.93	fine	11.41	6
66.88	9 fine Hs	39.88	8 b.h.	74.46	fine	12.88	7
66.99	6 fine Hs	40.86	9	74.93	8	13.57	7
70.45	7 b	41.60	9	75.55	fine	14.26	8
71.47	7	42.40	8 b	75.95	fine	15.09	fine
77.63	8 fine Hs	43.14	9 fine	76.55	7	15.90	9
81.43	10	44.01	9 fine	77.11	8	16.62	6 fine
82.32	8 b	44.92	9	77.77	7 fine	17.52	7 fine
83.35	H 10 b	45.83	8 fine	78.31	8	18.27	7
89.83	9 fine	46.84	10	78.93	8 fine	19.10	4
90.84	9 fine	47.98	7 fine	79.52	9	19.99	8 fine
93.00	10 fine Hs	49.12	7	80.16	8.5	21.66	6 b.h.
95.30	10 b	49.75	fine	80.80	9.5	22.52	6
99.30	10 fine	50.39	9	81.51	7 fine	23.40	2
4800.74	8 fine	51.00	fine	82.22	10	24.33	7
02.86	8 fine	51.61	9	82.93	7 fine	25.28	7
04.62	10	52.27	fine	83.63	10	27.11	faint
05.77	9	52.89	9	84.33	7 fine	28.14	7
06.46	6 fine	53.65	fine	85.17	8	29.13	7
07.20	9 b	54.35	9	85.88	8	31.22	7 fine
07.90	7 b	55.06	fine	86.59	8	32.20	7 fine
09.93	H 8 b.h.	55.74	9	87.42	7 fine	33.03	H 0.7
10.68	10	56.54	7 fine	88.18	9		wide
13.68	7 fine	57.32	7 b.h.	89.06	7	33.70	fine

WAVE-LENGTHS OF THE PRINCIPAL LINES AND BANDS IN THE ABSORPTION SPECTRUM — *Continued.*

GROUP A. λ 4600–5200.

Wave-Length	Character	Wave-Length	Character	Wave-Length	Character	Wave-Length	Character
4934.27	7	4970.74	8 fine	5002.55	7 fine	5034.36	fine
35.22	9	71.21	fine	06.31	fine	35.38	7 b
36.04	7	71.68	8 fine	06.90	7 fine	36.33	5 b
37.00	fine	72.09	fine	07.62	7 fine	37.34	8 fine
37.61	7 b.h.	72.61	8 fine	08.38	fine	38.17	fine
38.80	6	73.16	fine	08.78	7 fine	39.52	fine
39.54	7	73.70	7 fine	09.26	fine	40.02	fine
40.26	fine	74.28	fine	09.76	7 fine	40.94	H. b. 0.9
40.74	fine	74.40	8	10.24	7 fine		wide
41.29	fine	75.41	fine	10.68	7 fine	42.58	7
42.23	6 fine	75.98	8	11.26	7 fine	43.44	fine
43.16	7	76.61	7	11.77	7 fine	44.93	fine
43.82	fine	77.17	9	12.36	7 fine	44.59	fine
44.37	8	77.85	fine	12.83	7 fine	48.81	6
44.97	7	78.45	8	13.38	7 fine	53.39	6 Hs
45.53	fine	79.20	4	13.99	7 fine	53.49	10 Hs
46.10	7	79.91	6	14.50	7 fine	54.46	8 b.h.
46.72	7	80.56	7	15.13	7 fine	56.96	8 b.h.
47.49	7 fine	81.26	8	15.77	7 fine	58.34	7
48.07	7 fine	82.00	6	16.47	7 fine	58.97	7
49.24	8	82.65	7	17.06	7 fine	61.07	7
50.08	8	84.08	8	17.77	7 fine	62.79	7
50.83	fine	86.52	6	18.38	7 fine	63.38	8
51.50	8	87.18	6 fine	19.05	7 fine	64.11	fine
52.23	2 fine	88.19	6	19.68	6 fine	64.84	h
52.97	2 fine	88.98	10 b	20.42	8	66.69	7
54.39	10 b	90.90	5	21.14	6 fine	67.37	7
56.86	2	91.52	fine	21.89	8	68.29	b
57.70	2 fine	92.56	9 b	22.61	6	69.08	6 b
59.43	8	93.34	fine	23.37	7	69.82	7 b
60.15	fine	94.18	5 b.h.	24.18	6 fine	80.38	H 10 fine
61.06	6	95.15	4 fine	24.99	7	87.37	H 7 b
62.13	fine	96.11	fine	25.77	5	95.89	9 H
63.02	H	96.53	fine	26.33	7	5118.78	Hs b
63.80	f.h.	97.29	3 b	27.37	fine	26.84	b
64.88	10 b.h.	98.05	8 b	28.21	8	33.80	Hs b
66.81	fine	99.25	8	28.98	7 fine	41.27	Hs b
67.37	fine	5000.09	6 b	29.99	8		
68.79	8 b.h.	00.86	6	30.73	7 fine		
69.31	fine	01.84	H 0.7 wide	31.76	8		
69.77	7 fine		wide	32.53	6		
70.23	fine	02.17	fine	33.47	5		

GROUP C. λ5300–5700.

The lines of this group are all of about the same intensity and very faint. Only the strong lines of intensity 8 or greater are marked.

Wave-Length	Character	Wave-Length	Character	Wave-Length	Character	Wave-Length	Character
5269.38		5409.78		5572.53		5651.94	broad and strong 8
75.34		14.96		74.82			
79.58		16.52		75.90		52.80	strong
5305.68		18.90		76.81		54.27	strong
11.47		25.42		81.86		55.83	
17.65		26.20		83.07		59.97	strong
25.64		32.68		84.59		64.12	
30.61		33.63		93.45	strong 8	65.63	broad
34.85		39.25		94.87	strong 8	71.25	
37.70		40.33		5602.04	broad	72.68	strong 8
43.66		41.36		03.34	broad	79.03	strong 8
46.47		48.20		07.60		83.01	strong 8
49.67		52.94		12.31		84.30	
52.44		58.09		13.78		89.70	
58.36		63.11		19.09	strong 8	97.87	strong and broad 9
65.31		82.21		20.56	strong 8		
66.09		96.99		26.31	strong 8	5706.08	strong and broad 9
70.28		5502.48		28.13	strong 8		
71.23		23.48		32.79		10.84	strong 8
78.19		28.58		36.90		12.48	
82.12		30.44		38.02		13.56	
83.38		33.16		41.18		14.72	
84.33		35.89		42.26		17.23	
90.46		40.03		43.55	broad	18.05	
91.41		59.52		45.37	broad	20.82	
97.77		62.85		46.92	broad	34.78	
98.46		64.28		48.78		36.89	
5402.61		65.70		49.60		38.32	
03.90							

JOHNS HOPKINS UNIVERSITY,
Baltimore, June 1903.

THE SPECTRUM OF HYDROGEN.

By Louis A. Parsons.

Ångström[1] was the first to observe the hydrogen spectrum. In 1853, upon examining the light from an electric spark in hydrogen at atmospheric pressure, he noticed "an intense line in C not clearly limited, and two maxima in F and G; and a third maximum in *h* was observed later." Plücker and Hittorf[2] were the first to employ glass tubes with metallic electrodes and provided with capillary portions, and to study the spectra of gases at low pressure which were rendered luminous by an electric discharge. They found that the spectrum of some gases they examined was different when they employed a condenser in the discharge circuit of their induction coil, from that produced by the induction coil alone, and concluded that the former was due to higher temperature resulting from the condenser discharge. They obtained by means of the condenser discharge in hydrogen the three bright lines which they designated as *Ha*, *Hβ*, and *Hγ*. These lines they found expanded as the pressure of the gas was increased, and at high pressures the spectrum was transformed into a continuous one with *Ha* as a broad band rising from it. Without the condenser they observed another spectrum of hydrogen, "consisting of very many bright fine lines, especially in the neighborhood of the sodium line. This spectrum," they observed, "may be seen simultaneously with the three characteristic lines *Ha*, *Hβ*, and *Hγ*; but at increased temperature, when these lines begin to expand, it entirely disappears." With water vapor alone they obtained the lines *Ha*, *Hβ*, and *Hγ*.

There are now generally recognized two spectra of hydrogen: (1) the "elementary" or "four-line" spectrum, and (2) the many-line spectrum. The former includes the lines *Ha*, *Hβ*, *Hγ*, and *Hδ* in the visible portion, the last of which was soon added to the three given by Plücker and Hittorf, and nine lines in the ultra-violet. The many-line spectrum has also been designated

[1] *Phil. Mag.*, (4) **42**, 395, 1871. [2] *Phil. Trans.*, **155**, 1, 1865.

as the "compound spectrum" or the "secondary spectrum." The work of various observers has shown that the two spectra may exist together, and that in general as the lines of the elementary spectrum broaden the compound spectrum disappears. The question was early raised as to what caused the broadening of the lines, and what determined the presence of one spectrum or the other. Plücker and Hittorf, Wüllner,[1] and others[2] believed that the broadening of the lines and the change in the four-line spectrum was due to increased temperature. Others believed the effect was due to pressure,[3] and still others that the intensity of the electric discharge was the controlling factor.[4]

Trowbridge and Richards in 1897[5] found that a continuous discharge from their high potential storage battery of 5,000 cells, obtained by attaching the terminals directly to the electrodes of the vacuum tube with a high resistance in series, always gave a white glow in the capillary and the many-line spectrum of hydrogen, while the discharge from a condenser of considerable capacity gave the four-line spectrum, the color of the discharge being deep red. The introduction of self-induction, or of resistance to damp the oscillations, changed it back to the many-line spectrum. They believed that one spectrum was characteristic of the oscillatory and the other of the non-oscillatory discharge, the character of the electric discharge being the determining factor.

Further work, in which he employed his enlarged battery of 20,000 cells, however, led Trowbridge to abandon this idea[6] and to come to the conclusion that the many-line spectrum is the true spectrum of hydrogen, while the so-called four-line spectrum is due to water vapor; the existence of the four lines in the solar spectrum being, as he believed, due to the presence of water vapor in the Sun. His reasons for the conclusion were: (1) With powerful condenser discharges in apparently dry hydrogen he always obtained the four-line spectrum, and essentially the same

[1] *Phil. Mag.*, (4) **37**, 405, 1869. [2] FIEVEZ, *Comptes Rendus*, **92**, 521, 1881.

[3] SCHUSTER, *Brit. Assoc. Rep.*, **39**, 1873.

[4] STEARN and LEE, *Phil. Mag.*, (4) **46**, 406, 1873.

[5] *Phil. Mag.*, (5) **43**, 135, 1897. [6] *Ibid.*, (5) **50**, 338, 1900.

spectrum whether the tube was filled with nitrogen, air, or hydrogen, notwithstanding the greatest care taken in drying the tubes. He believed it was impossible to so thoroughly dry glass tubes as to remove all water vapor, and that the water on the glass is torn off by the powerful condenser discharges. (2) The four-line spectrum was easily obtained in all cases where water vapor was known to be present. (3) After a partial melting of the aluminium electrodes it was difficult or impossible to get the many-line spectrum (owing to the formation of compounds), but the four-line spectrum was obtained as easily as before with the powerful condenser discharges.

In a later paper Trowbridge[1] described some further experiments on high potential discharges through hydrogen. In one experiment, by using heavy copper electrodes he obtained by means of a continuous current a deposit of bright copper around the kathode and of oxidized copper at the anode, "the dissociation of the water vapor thus showing an electrolytic action closely analogous to that of a voltaic cell." He repeats his conviction "that the so-called line spectrum of hydrogen cannot be considered apart from the spectrum of water vapor," and is also "led to the conclusion that a certain amount of water vapor is essential to all electrical discharges through gases." He says: "Just as aqueous vapor seems to play an important rôle in most chemical reactions, so, it seems to me, its presence in rarified gases enables dissociation to take place which determines the strength and character of the electrical discharge;" and in another place: "The passage of electricity through a gas depends on the dissociation of the hydrogen and oxygen, by means of which change in the distribution of energy the gases are made luminous." While still holding that the four-line spectrum, as distinguished from the many-line one, is that of water vapor, he here advances to the idea that water vapor is essential to all electric conduction, in that it makes possible the passage of the current. During the passage of the current there may be produced the characteristic spectrum of the gas and also the spectrum of water vapor. In a recent article Trow-

[1] *Amer. Jour. Sci.*, **12**, 310, 1901.

bridge speaks of another spectrum of water produced by condenser discharges of great intensity giving a brilliant white light, which spectrum is continuous throughout the visible portion and consists of bands in the ultra-violet. These "spectra of water vapor" he believes are spectra arising from dissociation of water molecules.

J. J. Thomson in 1895[1] observed what appeared to be electrolysis of hydrogen gas in a vacuum tube, or the separation of positive and negative hydrogen ions. Using a tube with a metallic diaphragm, and allowing the current to run in one direction for some time, he obtained the *Ha* line strong on the positive side of the plate and *Hβ* faint, while the reverse was true on the negative side. His interpretation was that on the negative side there was an excess of positively charged hydrogen ions, and on the positive side of negatively charged hydrogen ions, the former having a natural vibration giving *Hβ* and the latter one corresponding to *Ha*. He also obtained by passing the current in one direction for a time through a mixture of hydrogen and chlorine, the hydrogen lines bright near the kathode and the chlorine lines weak or absent, and the reverse at the anode. This experiment was called in question by Morris-Airey[2] working in Kayser's laboratory, who believes that these effects were due merely to temperature differences. He employed two tubes, connected as shown in the figure, running a continuous current through a mixture of chlorine and hydrogen between electrodes *A* and *B* until the chlorine lines practically disappeared and the hydrogen lines became very bright at the kathode, and then

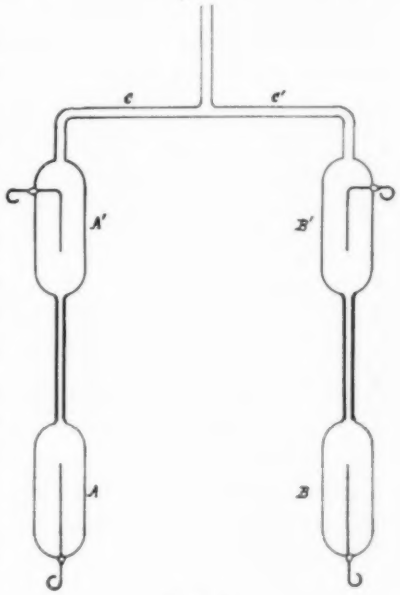


FIG. 1.

[1] *Nature*, **52**, 451, 1895. [2] *Phil. Mag.*, (5) **49**, 307, 1900.

he immediately sealed off the tubes at c and c'. Afterwards when they were used as separate tubes they gave identical spectra.

In a number of the *Philosophical Magazine* about a year ago, Lewis[1] discussed "the rôle of water vapor in gaseous conduction" suggested by Trowbridge's paper. He says: "It seems that the complete removal of water vapor from vacuum tubes is perhaps possible, and still the hydrogen or other gases contained therein may transmit the current and give their characteristic spectra." Deslandres, Wiedemann, and Lewis himself all found that by heating sodium in a tube containing hydrogen, although the hydrogen lines were weakened when the sodium vapor was dense, they came out with their full intensity when the sodium was cool. Using hydrogen with the same treatment, however, Deslandres succeded in getting rid of the water vapor lines. Lewis put pure sodium in a tube filled with hydrogen, and after heating it frequently to drive off impurities, he filled it with pure hydrogen, and then formed a "sodium dew" over the capillary and walls of the tube. Whenever it was heated the hydrogen lines were weak, but came out quite strong when the tube was cooled, and were just as strong after the tube had been used continuously for two weeks. When the tube was broken there were found large patches of sodium whose metallic surface was not tarnished, which led Lewis to observe that whatever other impurities might have been there, it is difficult to see how any free water vapor or oxygen could have been present." He concludes that "it seems at least doubtful whether water vapor is necessary to gaseous conduction."

Wilsing[2] recently made some interesting experiments on the spectrum of hydrogen. Making the usual observation that in general the introduction of a spark gap changed the many-line to the four-line spectrum and broadened the lines, he remarks that it cannot be an electrical resonance effect due to the oscillatory discharge, for the effect was not changed by varying the

[1] *Phil. Mag.*, (6) **3**, 512, 1902.

[2] "Investigations on the Spectrum of *Nova Aurigae*," *Pub. d. Astrophys. Observ. zu Potsdam*, **12**, 77–102, 1900.

period of the oscillation; and he comes to the conclusion that it is due to high temperature resulting from the condenser discharge.

A large number of the ultra-violet lines of the elementary spectra have been found as bright lines in the chromosphere of the Sun, but, on looking for their reversals, among the Fraunhofer lines of the solar spectrum, those of shorter wave-length $H\delta$ (H line) do not appear. The possibility of certain conditions of temperature or pressure in the photosphere being responsible for this suggests itself. Campbell[1] found that in the spectra of certain stars, the ultra-violet hydrogen lines are dark, while those of greater length are bright, there being a regular gradation between the two; and Kayser[2] calls attention to the fact that this is in accordance with the deductions of Kirchhoff's laws, assuming that they apply to this radiation.

Schumann[3] on examining the spectra of hydrogen from an end-on tube found, on varying the pressure, what appeared to be a reversal and a displacement of $H\beta$ or separation into components. Trowbridge[4] recently obtained a reversal of hydrogen lines in employing his intense condenser discharges, which he attributed to a selective reversibility of the silver salts of the photographic plate, and concluded that it was unsafe to draw conclusions from reversals as to the temperature, pressure or any other condition of the source, and considered this to have a very important bearing on astrophysical problems. Wood,[5] however, obtained effects entirely analogous to those of Trowbridge by subjecting a photographic plate to two light radiations, one of short duration and great intensity, followed by one of relatively great duration and feeble intensity (the Clayden effect); and he also found no selective reversibility in the silver salts, and concluded this could not have any bearing on astrophysical problems.

It is because of the bearing on astrophysical problems, the question of the physical condition and constitution of the heavenly bodies, that the determination of the exact conditions governing

[1] ASTROPHYSICAL JOURNAL, **2**, 177, 1895.

[2] *Ibid.*, **4**, 313, 1901.

[3] *Astronomy and Astro-Physics*, **12**, 159, 1893.

[4] *Phil. Mag.*, (6) **4**, 156, 1902.

[5] *Phil. Mag.*, (6) **4**, 606, 1902.

the changes in the hydrogen spectrum become of great importance. There are certain differences in the spectra of hydrogen as obtained in the laboratory and in the spectrum of the Sun and of the stars. Wright and Campbell,[1] from measurements of hydrogen lines in the spectrum of *o Ceti*, came to the conclusion that there was an error of one-tenth of an Ångström unit in the value of the wave-length of $H\delta$ given in Rowland's tables of the solar spectrum. The same conclusion has been reached by Evershed from measurements of the flash spectrum obtained in India during a total eclipse of the Sun. Jewell,[2] after carefully going over Rowland's measurements again, however, concluded that there was no error in the original calculation, the wave-length of $H\delta$ as a dark line in the Sun being 4102.00, while the value obtained by Evershed and by Wright and Campbell for $H\delta$ as a bright line in the Sun and stars (4101.85) agreed with the value obtained in vacuum tubes, which last also agreed with the place as given by Balmer's formula ($H\epsilon$ in the Sun also is not in accord with Balmer's formula).

Not all of the lines of the four-line spectrum of hydrogen appear in the dark-line spectrum of the Sun. Only $H\alpha$, $H\beta$, $H\gamma$, and $H\delta$ are distinct; those of shorter wave-lengths are of a different character—broad, hazy, and indistinct; and those of shortest wave-length are not distinguishable at all. This also is at variance with the four-line spectrum as ordinarily observed in the laboratory.

The elementary, or four-line, spectrum, according to the classification of spectra founded on the numerical relations and character of the lines, is not the principal but the first subordinate series. In 1897 Pickering[3] discovered another series of hydrogen lines in the spectrum of the star ζ *Puppis*, which according to Kayser[4] and Rydberg[5] constitute a second subordinate series following a different law from the first series, but ending at the

[1] W. H. WRIGHT, ASTROPHYSICAL JOURNAL, **9**, 50, 1899.

[2] ASTROPHYSICAL JOURNAL, **9**, 211, 1899.

[3] *Harvard College Observatory Circular* No. 12; ASTROPHYSICAL JOURNAL, **5**, 92, 1897, also **13**, 230, 1901.

[4] ASTROPHYSICAL JOURNAL, **5**, 95, 243, 1897. [5] *Ibid.*, **6**, 233, 1897.

same point in the spectrum. Rydberg also calculated the wave-lengths of the principal series of hydrogen, beginning at the same point in the spectrum as the second subordinate series. The second subordinate series, though observed in some stars, has never been obtained in the laboratory, and the principal series has never been observed at all.

The spectrum of hydrogen, then, is not by any means invariable; there are differences in the spectrum as observed in the Sun, in the stars, and in vacuum tubes in the laboratory; and in the latter there are observed changes due to different conditions of the discharge. Because of the bearing of the latter on the astrophysical problems involved, it becomes of great importance to accurately determine the causes of the changes we are able to bring about in the laboratory so as to have a guide in interpreting the particular variations in the spectra of the heavenly bodies. What, we are led to inquire, is the cause determining the occurrence of the four-line and the many-line spectrum, and of the changes in the spectrum as the conditions are varied? Is it high temperature, pressure, the electrical conditions of the circuit, or water vapor, or what? It was to obtain evidence to aid in answering these questions that the experiments described here were undertaken.

APPARATUS.

The hydrogen used in these experiments was prepared by the electrolysis of dilute sulphuric acid, and was passed through a system of tubes containing substances for drying and purifying to the Geissler tubes, and thence to another series of tubes to the mercury pumps used in exhausting, making a completely closed system about sixty feet long from generator to pump, with only one stop-cock at the generator. Calcium chloride, sulphuric acid, caustic potash, potassa-lime, and phosphorous pentoxide were used for drying, sulphur and gold foil for the removal of the mercury, and heated copper foil to remove oxygen. There was no trouble from hydrocarbon vapors, oxygen, or air after everything had been pumped out thoroughly, and most of the time there was no trouble from mercury vapor, the mercury lines not appearing in the spectrum, or else very faintly.

As a source for the electric current a storage battery of 4000 cells was constructed. For obtaining the continuous discharge the battery was connected to the vacuum tube with a water resistance of about a million ohms in series. A milliammeter was used to give the current. The oscillatory discharge was obtained by connecting the terminals of the battery to a glass plate condenser, equivalent to one or more Leyden jars, which in turn was connected through a spark-gap and coil of self-induction of 0.009 henry (which coil could be short circuited at will) to the vacuum tube.

FIG. 2.

A number of tubes were used of different diameters and with different distances between the electrodes, and the spectrum was observed with a Steinheil spectroscope as the pressure of the gas, the temperature, and the electrical conditions of the circuit were varied. Some of the tubes had capillaries, but most of them had none, being of uniform diameter of from 6 to 22 mm. The electrodes in most cases were of aluminium rod 2 mm in diameter. The pressure of the gas was varied from nearly an atmosphere down to a millimeter (and sometimes a fraction of it).

CONTINUOUS DISCHARGE — EFFECT OF PRESSURE.

The continuous current of a few milliamperes from the battery always gave the many-line spectrum and the four lines all sharp and fine even at the highest pressures (500 mm, or even 700 mm). The discharge in wide tubes was characterized by a bright point on the anode (which appeared always to give the many-line spectrum), and a white velvety glow at the kathode, which appeared on the tip of the electrode at high pressures and gradually expanded until it filled that part of the tube at a pressure of a millimeter, and in which $H\beta$ could always be seen. There was no essential difference in the action of the tubes with different electrode distances, as the pressure was lower; the discharge ceased sooner in the tubes with the electrodes close together than in those with electrodes farther apart. In the capillary the spectrum was faint at high pressures, appearing first in

the green and blue, with $H\beta$ not as bright as other fine lines in that region. With decreasing pressure the spectrum first spread toward the red and violet, and then the intensity of the whole increased, and also the relative intensity of the four lines, until the point of maximum resistance was reached, beyond which the process was reversed.

VARIATION OF CURRENT DENSITY.

The same changes that occur in the glow discharge and in the spectrum during a decrease of pressure were produced by increasing the current either by an increase of voltage or a decrease of external resistance, but the changes also took place with decreasing pressure at constant current (though less rapidly than with decreasing pressure and constant external resistance).

The abruptly oscillating discharge, occurring with the condenser and spark-gap, gave the deep red spark discharge between the electrodes, and always tended to broaden the lines and to increase the relative intensity of the four lines. At high pressures, with considerable capacity, the four lines appeared very bright and broad, while the *Al* lines from the electrodes were bright and fine. With decreasing pressure the four lines gradually became narrower, $H\alpha$ first becoming fairly sharp, and then $H\beta$. All decreased in intensity, but $H\delta$ faded away relatively quite rapidly. The electrode lines disappeared in the central portion, and finally extended only a short distance from the electrodes. At a pressure of more than 100 mm the many lines appeared in the red and orange, at first broad and indistinct and massed together, but sharp and distinct at lower pressures. With decreasing pressure the many lines increased in intensity relatively to the four lines. The introduction of self-induction even at pressures as high as an atmosphere made the four lines narrow, and brought out the many lines quite distinct and fine. Excepting at very high pressures, self-induction increased the intensity of the many-line spectrum, and decreased the intensity of the four lines.

A tube 15 mm in diameter, with electrodes 6 mm apart, showed a heavy red spark discharge at high pressure, which,

when the pressure was lowered to about 100 mm, contracted to a cone with its base at the anode and extending almost to the kathode, and was surrounded by a blue sheath broadest at the kathode. The blue glow gave a faint continuous spectrum and, apparently, the many-line spectrum of hydrogen, though faint.

FIG. 3.

The red discharge gave the four lines broad and bright near the electrodes, Ha and $H\beta$ extending all the way across and rather fine near the kathode, while $H\gamma$ and $H\delta$ were seen only near the anode. With decreasing pressure the red cone shortened until it became a point on the tip of the anode, and finally disappeared, leaving the discharge entirely blue. Another tube of a larger diameter, but in all other respects identical with this one, gave the deep red discharge throughout this entire range of pressure. It was at first difficult to see how two tubes, both connected to the apparatus and at precisely the same pressure, and differing only in diameter (and in that very slightly), would act so differently. It was easily shown, however, that the resistance of the tube was the determining factor, being high enough in the narrower tube to prevent the abruptly oscillating discharge which took place easily in the larger one. When a high external resistance was put in series with the large tube, it gave the blue discharge similarly to the narrower tube, and when the capacity was increased the red discharge occurred in the narrow tube at comparatively low pressures. In fact, in all the experiments, whenever the electrical conditions of the circuit were such as to give the abruptly oscillating discharge, the red discharge and the four-line spectrum resulted. Tubes of different diameters were employed, but they showed no differences, excepting in so far as the greater resistance of the narrower ones causes the change to the blue spectrum at higher pressures.

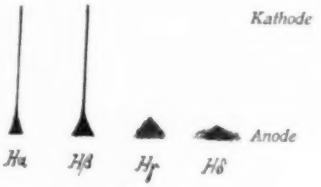


FIG. 4.

EFFECT OF HEATING.

If the four-line spectrum is due to water vapor, one might expect an external heating of the tube sufficient to drive off water vapor, to cause an increase in the red discharge, and a corresponding increase in the intensity and width of the four lines. Or if the four-line spectrum is due to high temperature (of the gas as a whole), we should look for the same effect when the tube is heated. However, heating the tube externally by means of a Bunsen burner, or internally by continuing the discharge for some time, instead of having the effect of increasing the amount of red in the discharge and producing a change in the direction of the four-line spectrum, had the opposite effect, decreasing the red or changing to the blue discharge.

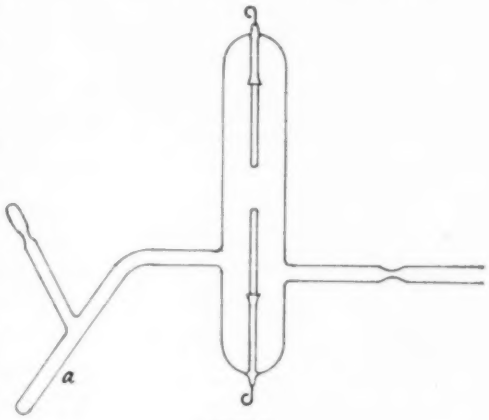


FIG. 5.

EFFECT OF WATER VAPOR.

Two tubes, as nearly identical in all respects as possible and of the form shown in the adjoining figure, were connected, one, *A*, directly to the apparatus, and the other, *B*, through drying tubes of calcium chloride and phosphorous pentoxide. In the bulb of *B* was placed about $\frac{1}{10}$ cu. cm of water, which was kept frozen while the tubes were being exhausted, washed out, and filled with hydrogen. The pressure was lowered to 44 mm, when the discharge was blue, with red extending only a short distance from the tips of the electrodes, and identical in the two tubes. The ice was melted and a short time allowed for the water to evaporate. No effect was observed then or when the water was slightly warmed. But when the water was boiled so that some passed over into the main tube, the discharge in *B* became red all the way across, and *Ha*, *Hβ* and *Hγ* became much brighter.

The discharge remained very decidedly red after running for some minutes, when it was certain that the pressure was the same in the two tubes. Tube *A* gave the blue discharge with the red on the tips of the electrodes, just as before. On cooling the side tube in the freezing mixture, the discharge became decidedly less red. When nearly all of the water was boiled over into the main tube, the discharge became very red, and $H\alpha$ and $H\beta$ came out very bright and broad, $H\gamma$ was broad, and $H\delta$ seemed to be present, faint, and broad. On again placing the side tube in the freezing mixture and passing the current through it, the discharge became decidedly less red, and finally became somewhat blue, though not as much as the other tube.

The experiments appear to show a very marked connection between the four-line spectrum and the presence of water vapor or water. But it is to be noted that the effect was produced only when water or water vapor was present in large quantities, and did not appear in the least with only small traces of the vapor. With large quantities present some evidently was on the electrodes and in the path of discharge, and the vaporization and dissociation of the water by the current would produce a high local increase in the pressure; and the effect observed was exactly that which would have been brought about by an increase in pressure. Or, the sudden ionization of the water might well produce a violent change in the passage of the electric current—causing the abruptly oscillating discharge of which the four-line spectrum was characteristic.

When one of the tubes cracked, the presence of the air leaking in was shown by the oxygen and nitrogen bands. With the discharge without the condenser, or with the condenser and self-induction, most of the current was carried by the nitrogen, scarcely anything else being seen in the spectrum excepting the nitrogen. With capacity without self-induction and with a small spark-gap, the oxygen predominated, while with a large spark-gap giving a very definite disruptive discharge the current was carried almost entirely by the hydrogen, the four lines coming out brilliantly.

DISCHARGE IN AIR.

A system of four tubes varying in diameter from 6mm to 22mm, all with electrodes about 7mm apart, and a bulb 90mm in diameter, with electrodes 10mm apart, were first used, when filled with air, before any hydrogen had been admitted. Excepting at quite low pressures, the walls of the bulb were so far away from the discharge as not to be at all heated or apparently affected by the discharge in any way. In the narrower tubes, where the discharge reached the glass walls, *Hα* and *Hβ* were seen very bright (especially *Hα*) and broadened throughout a great range of pressure, while they were not seen at all under like conditions in the bulb. This pointed very strongly to the conclusion that the four-line spectrum is due to water vapor driven from the walls of the tube. But although *Hα* was bright in the narrower tubes, *Hβ* was usually comparatively faint, *Hγ* was never seen with certainty, and *Hδ* not at all. When the tubes were filled with dry hydrogen, it is not likely that they contained more water vapor than when filled with air from the room, and yet, with the hydrogen, all the tubes, including the bulb, showed with the condenser discharge *Hα*, *Hβ*, *Hγ*, and *Hδ*, all very bright and broad. The four-line spectrum was plainly not the same in air as in hydrogen, and certainly the evidence was not in favor of the assumption that the four-line spectrum is due only to water vapor and not at all to hydrogen as such.

It may be, as Trowbridge claims, that "a certain amount of water vapor is essential to all electrical discharge through gases," and that the four-line spectrum of hydrogen is intimately associated with the dissociation of water vapor. The idea that a perfectly dry gas of any kind not ionized is a non-conductor of electricity is certainly not a new one. In a paper published in the *Philosophical Magazine* in 1893,[1] J. J. Thomson considered the effect upon the formation of drops and said: "In a vacuum tube with electrodes at high potential, the presence of the electric charges would tend to form drops of water, if there should be any water vapor present;" and he concluded that the mole-

[1] (5) **36**, 313.

cules might be dissociated into charged ions by condensation on the surface of little spheres of water or of any other liquid of high specific inductive capacity, and these charged ions in turn would facilitate the formation of other drops of water. This action would render easy the passage of a current from one electrode to the other. The presence of water vapor in this way would tend to ionize whatever gas were present in a vacuum tube, and thus render possible the passage of a current and put it into a condition to vibrate in such a way as to give its characteristic spectrum. But it cannot be said that water is absolutely necessary for this, for the same might be done by any liquid of high specific inductive capacity. In fact, anything that could ionize the gas in the tube, as X-rays, Becquerel rays, ultra-violet light, or the *Entladungstrahlen* from a spark, would render the gas conducting, and in a perfectly dry gas, not ionized with high enough potential, we may obtain a disruptive spark discharge. And a gas that from any cause whatever is carrying electricity through it, it seems fair to assume, may be giving off its characteristic spectrum, entirely apart from the presence of water vapor or any other foreign substance.

As stated before, some of the experiments described in this paper, as well as the experiments of Trowbridge, point to a connection between water vapor present in a tube and the four-line spectrum of hydrogen. It does not seem, however, that one is warranted in concluding that the four-line spectrum is the spectrum of water vapor. It may be that this spectrum is due to the particular vibrations produced at the instant of dissociation of water molecules, or of recombination of hydrogen and oxygen ions. But may it not even in that event be that the four-line spectrum is a true spectrum of hydrogen, which is due to the particular vibration of the hydrogen ion occurring at the instant of ionization, which ionization may be that of a hydrogen molecule, or of a molecule of any other compound of hydrogen as well as of water, while the natural vibrations of the free hydrogen ion give rise to the many-line spectrum? The experiments stated in this paper could be explained in this hypothesis, and could not the experiment of Trowbridge as well?

But we are not excluded from the possibility that pressure or the electrical conditions of the circuit are the determining factors. This much seems certain, whenever the discharge is comparatively steady, as with a battery, the many-line spectrum is produced, while the abrupt oscillating discharge always gives the four lines bright. The presence of water vapor in quantity (as in one of these experiments) would in the electric field result in the formation of drops of water, the vaporization and the dissociation of which would, as has been stated, cause great local increase of pressure, which would account for the facts observed, if we consider it a pure pressure effect.

The most natural conclusion from this investigation is that the four lines are increased in intensity and in width whenever anything occurs that renders the electrical discharge discontinuous and very abrupt and violent. As to what the process or mechanism is by which the characteristic mode of vibration is produced, whenever this occurs, we cannot say.

A series of photographs of the hydrogen spectrum were taken with a quartz spectrograph with capacity and self-induction, at pressures ranging from about 700 mm down to 2 mm, which gave results in harmony with the eye observations already noted. A point of interest that attracts one's attention in looking over the plates is that the lines $H\epsilon$, $H\zeta$, $H\eta$, $H\theta$, etc., assigned to the four-line spectrum, are either not present at all or else do not seem to behave in the same way as $H\alpha$, $H\beta$, $H\gamma$, and $H\delta$, which are very intense and broad at high pressures, and gradually decrease in width and intensity with decreasing pressure; while the others are faint and narrow at high pressures and change very slightly if at all with decreasing pressure.

CONCLUSIONS.

1. The "compound spectrum," "secondary spectrum," or "many-line" spectrum of hydrogen never occurs without the four lines. The four-line spectrum may occur at high pressures without the many lines.

2. The four-line spectrum is characteristic of an abruptly oscillating discharge, and the many-line spectrum of the contin-

uous discharge of the battery, the less violent oscillatory discharge which occurs with self-induction in the circuit giving a spectrum midway between the two—the many-line spectrum with the four lines very bright and fine.

3. The production of the four-line spectrum, or the broadening of the lines, may be due to high temperature occurring along the path of discharge, or locally at points where the disruptive discharge takes place, *i. e.*, it may be due to an increased translatory motion of the particles which have this mode of vibration—a point which it seems impossible to determine. But it seems certain that this is not due to high temperature, if we mean the average temperature of the gas in the tube.

4. It is likely that the presence of water vapor in a tube plays an important rôle in the conduction, because of its effect in ionizing the gas, but it seems also likely that other agencies may produce the same result. There seems to be a connection between the presence of a quantity of water vapor and the brightness of the four lines, and it may be that the process of dissociation of water gives rise to vibrations producing the four-line spectrum. But there does not seem to be any evidence for saying that the four-line spectrum is the spectrum of the water vapor. On the contrary, the "four lines" appear to be true lines of hydrogen.

In conclusion I wish to acknowledge my obligation to Professor Ames, at whose suggestion the work was undertaken, for the kindly and helpful interest he has always shown; to Professor Wood, for his suggestions; and to students who have assisted me, particularly Mr. George W. Middlekauff, who was for a considerable time associated with the work.

JOHNS HOPKINS UNIVERSITY,
May 1, 1903.

SOME EFFECTS OF CHANGE OF ATMOSPHERE ON ARC SPECTRA WITH REFERENCE TO SERIES RELATIONS.[1]

By A. S. KING.

SINCE the discovery of series relations in the spectra of a number of elements, those investigators who have studied the changes produced in such spectra by variation of physical conditions have noted in many cases that lines belonging to a series are affected differently from the unrelated lines; and that when two or more series are present, they may be affected in different ways by change of condition. Such changes in physical conditions not only furnish us with a means of separating the lines of an element into groups between the members of which series relations may be looked for, but we may be enabled to draw conclusions as to the character of the vibrations which give rise to such lines by observing what conditions seem to be most favorable for their production. Any points which can be established in regard to these matters will be of great use in astronomical investigations, where the spectra of heavenly bodies show many differences in relative intensities of lines, which, if explained, would give indications as to the condition on these bodies.

The influences upon spark and arc spectra of changes in temperature, pressure, nature of discharge, and by a magnetic field have been observed, and the tendency of such changes to affect certain lines more than others has been frequently noted. Another method of separating lines into groups is the use of different gases around the electric arc or in the tube through which a spark is passed. It has long been known that such changes of atmosphere may affect certain lines in the spectrum of an element more than others, but it is only recently that any notice has been taken of the method as a means of grouping related lines.

[1] Extract from a dissertation presented in partial fulfilment of the requirements for the degree of doctor of philosophy in the University of California.

The work of Professor Crew[1] with metallic spectra influenced by an atmosphere of hydrogen has shown that the lines belonging to Kayser and Runge's series are unaffected by a change from air to hydrogen in the cases of the metals he investigated, and he points out that the use of hydrogen may offer a means of dividing spectra into series and non-series lines. R. A. Porter[2] has supplemented Professor Crew's work by the use of oxygen, nitrogen, and ammonia with several metallic arcs, but his results relate chiefly to the changes in prominent spark lines. The method thus seems to be only in the beginning of its usefulness.

The work of which an account is to be given was undertaken for the purpose of making a systematic study of the arc spectra of several metals whose lines show regularities in their arrangement, with reference to changes produced by the atmosphere surrounding the arc. The attempt has been made to connect the observed changes with the series relations among the lines of the metal, to separate the lines into groups by this means, and to deduce general conclusions as to the nature of the physical conditions which bring about the observed effects.

With this object in view, a detailed study has been made of the spectra of calcium, strontium, barium, and copper, with the arc in atmospheres of air, oxygen, carbon dioxide, nitrogen, ammonia, and the vapors of mercury and sodium. A few observations have been made of the spectra of magnesium and zinc. The use of copper terminals in some cases has given an opportunity to observe the effect of copper vapor mixed with that of the metal under observation.

Carbon terminals were used for most of the work with the metals of the calcium group. The chlorides of calcium, strontium, and barium were used, and powdered magnesium. Carbons made from calcined sugar by the method previously described[3] were used to advantage in some cases by mixing the metallic salt or powder with the powdered charcoal, then molding and baking the compound. This gives a very uniform distribution of the metal through the carbon and freedom from impurities found in the

[1] ASTROPHYSICAL JOURNAL, **12**, 167, 1900. [2] *Ibid.*, **15**, 274, 1902.

[3] A. S. KING, ASTROPHYSICAL JOURNAL, **14**, 323, 1901.

commercial carbons. Calcined rock-candy has been found to give a very pure carbon for this purpose. In using calcium chloride it is difficult to get enough of the metal in the carbon, as a large amount causes the carbon to disintegrate in the baking. Furthermore, carbons containing any hygroscopic salt must be used at once after baking, as the absorption of water vapor causes them to go rapidly to pieces. When a large amount of metal in the carbon was desired, commercial carbons were used, with their cores bored out and filled with the metallic salt or magnesium powder. These were satisfactory for the most of the work, as the spectrum showed but few impurity lines. In cases where it was desirable to eliminate the carbon spectrum, or to observe the effects of copper vapor, copper rods were used as electrodes, their ends being bored out and filled with the metallic salt.

In order to try the effects of sodium and mercury vapors, the lower carbon was passed through the bottom of a small graphite or clay crucible which was fitted around the carbon a short distance below the end, and filled with metallic sodium or mercury. The arc being started, the heat caused the sodium or mercury to give off large quantities of vapor. The use of sodium vapor with carbon terminals causes the lower carbon to disintegrate rapidly where the liquid sodium comes in contact with it, possibly on account of the presence of water in the interior of the carbon, which is attacked by the sodium. This action on the carbon limits photographic work to short exposures.

During the first part of the work the inclosure used for the arc was a glass bulb made from a round-bottomed flask by introducing a tube into a hole blown in the bottom. Stoppers were placed in this tube and in the neck of the flask, through which carbons were passed, also tubes for the passage of gases. With this chamber, either the vertical or the horizontal arc could be used. Later a heavy graphite crucible 10cm in diameter was used for the chamber. This was made almost gas-tight by inverting it upon an asbestos base through which the lower carbon and the inlet tube for gases were passed. The upper carbon and outlet tube entered through holes in the top, and the light from the arc passed through a hole in the side 1cm in diameter, over which a glass or quartz window was placed.

The spectrum was formed by a fifteen-foot Rowland concave grating, of which the first order spectrum was usually used. Comparison photographs were made on the same plate, usually four in number, the two outer with the arc in air with different lengths of exposure, the two inner with the arc in the gas or vapor whose effect was being studied, and with exposures corresponding to those for air. An effort was made to avoid overexposure, which would tend to equalize the intensities of lines.

CALCIUM.

The spectrum of calcium has been photographed by the writer, with the arc in atmospheres of oxygen, carbon dioxide, nitrogen, ammonia, and the vapors of sodium, mercury, and copper. The fact that the calcium salts are very volatile in the arc makes it difficult to control the conditions as to the amount of calcium vapor present in the arc. We cannot know that the same amount of calcium was fed into the arc for each of two comparison photographs, so that a general strengthening of the lines under certain conditions of surrounding atmosphere means little. It seems useless, therefore, to make any statements as to the absolute effect of a certain atmosphere on the calcium spectrum, and so I have considered only relative differences, and have looked for the causes which produce a greater intensification of some lines than of others when conditions are changed.

The most striking relative difference appears when we compare the behavior of the ultra-violet triplet of wave-lengths 3644.45, 3630.82, 3624.15 with a pair of sharp lines at λ3737.08 and λ3706.18. The triplet is a member of the first subseries of Kayser and Runge. The pair does not belong to a series, but has the same difference in wave-number (223) as the H and K lines, and almost the same as the pair at λ3179.45 and λ3158.98 (204). The triplet and pair just mentioned are close together, can be easily compared, and are observed to be affected differently by a surrounding atmosphere in nearly every photograph of the large number I have taken. The pair at λ3179.45 and λ3158.98 behaves very similarly to the pair just mentioned.

The action of the H and K lines is similar in a general way, but they seem to change more easily than the other pairs, perhaps on account of greater strength and frequent reversals. The changes in the triplet at λλ3644.45, 3630.82, 3624.15 are a type of the behavior of the more diffuse lines of the spectrum, including the triplets belonging to Kayser and Runge's series and most of the unrelated lines. Triplets belonging to the second subseries show a change in the same direction, but not always to the same degree as those of the first subseries. Lines belonging neither to the series nor to the pairs mentioned above show an effect intermediate between that of the sharp lines of the pairs and that of the triplets of the first subseries.

Taking the pair and the triplet as types of the two kinds of lines into which the calcium spectrum may be divided, let us notice first the effect of varying quantities of calcium in the arc, other conditions remaining the same. With a very little calcium in the arc, the pair and triplet are of about the same intensity and both sharp. Sometimes the pair is stronger than the triplet. On increasing the quantity of calcium in the arc, the pair increases but slowly in intensity and remains sharp. The triplet, on the other hand, rapidly becomes strong and diffuse, the lines broaden toward the violet, and with a large amount of calcium reverse. This behavior is typical of that of all triplets belonging to the two Kayser and Runge series, the action being most pronounced in the case of the more hazy triplets, as those whose strongest lines are at λλ3361, 3487, and 4099.

It appears, therefore, that the increase of vapor density, which should result from an increased supply of calcium, would account for the broadening observed in the case of the more diffuse lines, and that the sharp lines do not show a corresponding increase in intensity. An increase in vapor density is probably accompanied by an increase in the temperature of the arc, since when the arc is started with a large amount of the salt in the carbon, the current is above normal, and other conditions which relatively enhance one set of lines usually give a slight increase in current.

This selective effect of change in density makes it difficult to

form tables of relative intensities for spectra like that of calcium whose lines do not all behave alike. I have often noticed that the relative intensities of lines on my plates do not correspond with those given by Kayser and Runge. For example, the latter give the intensities of the lines forming the triplet λλ3644, 3631, 3624 as 1, 2, 2 respectively, and the lines λ3737 and λ3706 each as 4. The arc in air does not give this relation unless a large amount of calcium is used, as was probably done by Kayser and Runge in order to have all of the calcium lines appear distinctly.

If we now observe the effects of various atmospheres upon the calcium spectrum, we find that the theory of change of relative intensity in certain lines by increased vapor density is the only one which will harmonize the effects of change of atmosphere with the observed effects in air when the amount of metal consumed is changed. Consider first the effect of oxygen. Oxygen greatly increases the consumption of metal in the carbon arc. The carbons waste away rapidly and a large amount of calcium oxide is formed. The arc is very luminous; the current usually increases one or two amperes from its value with air around the arc. The effect on the spectrum is to enhance the diffuse triplets much more than the sharp lines which do not belong to series. This is especially noticeable in the case of the triplets with lines of greatest wave-length at λλ3361, 3487, 3644, 4099, 4586, as compared with the sharp lines λλ3159, 3179, 3706, 3737, and the group from λ4283 to λ4319, which do not broaden readily. The H and K lines are strengthened, but not so much as the *g* line, the reversal of which is widened. There is no essential difference, however, between these effects and those given by the arc in air with a large amount of calcium present. I am not now taking up the question as to whether oxygen really increases the *absolute* intensity of the calcium lines. That could be tested only by an arc formed between terminals of metallic calcium and with a constant current. The greater amount of calcium consumed by the arc in an atmosphere of oxygen would account for the general strengthening.

The effect of carbon dioxide on the calcium spectrum is very

similar to that of oxygen, but not so decided. It is probable that large quantities of carbon dioxide are generated by the use of oxygen around the carbon arc, as the oxidation rapidly reduces the diameter of the carbons.

Turning now to the effects of some atmospheres which exclude oxygen to a greater or less degree, we shall consider first the atmosphere of pure nitrogen. This was prepared from ammonium sulphate and sodium nitrite, and purified by passage through sulphuric and pyrogallic acid. Its effect seems to be to prevent oxidation without decreasing the vapor density to any great extent. The arc burns readily in nitrogen, and the same time of exposure can be used as with air or oxygen. The carbons are consumed very slowly, and no calcium oxide is formed if a strong current of nitrogen is maintained. Still, from the ready burning of the arc, it is not probable that the vapor density in the arc is greatly different from the conditions in air, and it is different from the conditions in oxygen chiefly because with the latter gas more calcium is supplied to the arc in a given time.

The effects with nitrogen are entirely in accordance with this view. The tendency of nitrogen is to equalize the intensity of the pair and triplet considered above as types of the two sets of lines. The vapor density is probably small, but not smaller than we can obtain in air with a small amount of calcium and a strong current of air pumped through the chamber. In some photographs where a large amount of calcium was used with nitrogen atmosphere, the triplets were broadened and rendered diffuse in a way often observed in air and approaching the effect of oxygen. The fact that this broadening is possible under some circumstances with a strong current of nitrogen around the arc is very much against the theory that the broadening is due to oxidation, or due in any large degree to higher temperature, as we should expect the violent combustion in the oxygen atmosphere to raise the temperature of the arc as well as that of the electrodes.

The use of sodium vapor around the arc gives another test for the effect of increased vapor density without oxidation. A

stream of sodium vapor passing up on all sides of the arc from a cup of boiling sodium around the lower carbon would allow but little oxidation, while it might be expected to crowd the calcium vapor back into the arc and increase the vapor density in the arc. The photographs taken under these conditions show a decided difference in effect upon the two sets of lines, and the difference increases as the sodium vapor becomes denser. With the sodium boiling vigorously, the pairs remain sharp and show little change in intensity, while the triplets become broad and diffuse, and the reversal of *g* is much widened. The sodium vapor increases the conductivity of the arc so that the current is greater than with air and the electrodes are consumed more rapidly, a condition which should lead to an increase of vapor pressure. An explanation may thus be given for the observed fact that the effect of sodium vapor is much like that of oxygen, though we might expect the opposite.

Turning now to the effect of ammonia, we have here a gas which in all probability reduces the vapor density in the arc. As has been observed by others, the arc is very difficult to maintain in ammonia. When it is burning, the current and fall of potential show little change from the conditions in air, but the intensity is feeble and the arc is often extinguished. The exposure must be from twelve to twenty times as long as with the arc in air. With a strong stream of ammonia sweeping away the gases formed in the arc and the feeble action which we observe, the conditions seem very favorable for a minimum vapor density in the arc. None of the other atmospheres I have used give such a relative weakening of the lines belonging to Kayser and Runge's series as compared with the pairs at λ3159 and λ3179, λ3706 and λ3737, and the H and K lines. The pairs mentioned are stronger than in air in the case of several photographs in which the supply of calcium was kept the same as nearly as possible. The triplets, on the other hand, are very decidedly weakened, and their lines rendered sharper. The reversal of *g* is much narrower in ammonia; also that of H and K, when they are reversed. The effect of mercury vapor around the arc is to diminish the triplets more than the pairs. The *g* line shows a

narrower reversal, and the effects all point toward a lower vapor density than with the arc in air. The poor conductivity of mercury vapor may account for this, giving the effects observed to a much greater degree in the case of ammonia.

The use of copper electrodes with calcium filling gives another means of producing conditions in which the vapor density is probably small. The copper arc is of feeble intensity, a much longer exposure is needed than with the carbon arc to make the lines equally strong, and then relative differences appear in the two sets of calcium lines much like those observed when mercury vapor was used around the arc. Comparing two photographs of the calcium spectrum between λ3500 and λ4600, one with carbon and the other with copper electrodes, with the H and K lines, as well as the pair at λ3737 and λ3706 of the same intensity in both, we observe a very distinct difference in the behavior of the other calcium lines. The several triplets are much weaker in the copper arc, the greatest difference being in the diffuse triplets with lines of greatest wave-length at λ3644 and λ4512. The *g* line is narrow and not reversed in my plates taken with the copper arc.

STRONTIUM.

The spectrum of strontium has been studied by the writer from λ3000 to λ5000 with atmospheres of air, oxygen, carbon dioxide, nitrogen, ammonia, and sodium vapor. The relative differences found result in the segregation of a group of strong lines which make up three pairs having the same difference in wave-number, given by Kayser[1] as follows:

λ		Vibration-Difference
4305.60		
	- - - - - - -	801.6
4161.95		
4215.66		
	- - - - - - - -	801.5
4077.88		
3475.01		
	- - - - - - -	801.1
3380.89		

These are homologous to the three pairs in the calcium spectrum which were observed to be affected by surrounding atmos-

[1] *Handbuch der Spectroscopie*, **2**, 541,

phere differently from the lines belonging to Kayser and Runge's series. In the strontium spectrum we again find a difference in the effect upon these two classes of lines; but in this case it is the sharp lines forming the pairs which are the more sensitive to changes of physical condition.

A comparison of a large number of photographs shows conclusively that the lines of these pairs are strengthened by atmospheres of oxygen, carbon dioxide and sodium vapor to a greater degree than the remaining lines of the spectrum, and are correspondingly weakened by atmospheres of nitrogen and ammonia. The sharp line at λ3464.58 is acted upon in the same way as the pairs, but seems to have no companion with a similar behavior. The broad reversed line at λ4607.52 is not strengthened by oxygen to the same degree as the pairs. In carbon dioxide it is actually weaker than in air, while the pairs are much stronger, and the remaining lines, including those belonging to Kayser and Runge's series, show little difference. In ammonia λ4607.52 sometimes suffers a double reversal, making it broad and hazy. The pairs are distinctly weakened by ammonia, giving a general effect opposite in character to that of the first three gases. The action of nitrogen is similar to that of ammonia, but not so pronounced, as the pure nitrogen seems to make but a slight change from the conditions of the arc in air.

A NEW STRONTIUM TRIPLET.

In studying the spectrum of strontium, the writer has observed that whenever the line λ4077.88 is of considerable intensity, three faint lines appear close to it. The wave-lengths of these three lines I have measured as follows:

4087.86
4071.22
4061.52

Not being able to identify these with any known metallic lines, I have applied several tests to determine whether they belong to strontium, to some impurity, or whether they may be "ghosts" of λ4077.88. The last possibility was easily settled. The three lines are not at all symmetrical with respect to

λ4077.88, but a decisive test was made by comparison with the prismatic spectrum. A train of prisms was arranged which gave a dispersion almost equal to that of the first-order grating spectrum, and the three lines came out quite as strongly as with the grating. It is very improbable that they are due to metallic impurities, as they are given by "chemically pure" preparations of both the chloride and the nitrate of strontium, in a carbon arc with very pure carbons made from calcined sugar. Again, it is not likely that the lines are the heads of strontium oxide bands, as they are not reduced in intensity by atmospheres of nitrogen or ammonia.

While my measurements agree very closely with the wave-lengths of three carbon lines given by Kayser and Runge as λλ4087.88, 4071.13, 4061.53, the three lines first mentioned are certainly not carbon lines in their normal condition, as they stand out distinctly only when strontium is present.

Perhaps the strongest evidence that the three lines belong to strontium is the fact that they form a triplet having the same differences in wave-number between the component lines as the differences for four strontium triplets given by Kayser and Runge.[1] These triplets do not belong to a known series, and have their lines much closer together than the series triplets. The four triplets with their vibration-differences are as follows:

λ	Vibration-Difference
5535.01	100.2
5504.48	60.0
5486.37	
5257.12	100.4
5229.52	59.8
5213.23	
4892.20	97.7
4868.92	57.8
4855.27	
4338.00	99.3
4319.39	58.6
4308.49	

[1] *Abh. Berl. Akad.*, 1891, p. 34.

The fifth member of this group of triplets seems to be the three lines:

4087.86		100.0
4071.22	- - - - - - -	
4061.52		58.6

The members of these five triplets are the more diffuse lines in the strontium spectrum. There is a decided similarity in appearance between the last two triplets, though the one to which I have called attention is much the weaker.

MAGNESIUM.

The writer has made but few observations of the spectrum of magnesium, and these have for the most part given negative results, as far as relative differences are concerned. This may be due to the fact that nearly all of the prominent lines belong to the triplets of the first and second subseries of Kayser and Runge, and so may be expected to show the same behavior with change of physical conditions. The spark line λ4481 does not appear in my photographs.

My plates show a very slight difference in the behavior of the triplets belonging to the first subseries in atmospheres of oxygen and nitrogen from that of the second subseries in the same atmospheres. The triplets of the first subseries are relatively stronger in nitrogen, those of the second subseries in oxygen. This is the case with the triplets with lines of greatest wave-length at λλ 3838, 3097, 2852 of the first subseries as compared with those at λλ 3337, 2942, of the second. The difference is most noticeable in the case of the very broad line λ2852. The results so far obtained do not point to any more general conclusions than the similar behavior of lines belonging to the same series.

BARIUM.

A study of the spectrum of barium with the arc in atmospheres of air, oxygen, nitrogen, carbon dioxide, ammonia, and the vapors of copper, mercury, and sodium, shows a number of lines which are affected differently from the majority of the barium lines, and always affected in the same way by a given gas. While no

general series relation has yet been found for the barium lines, my results serve to strengthen the evidence that certain lines are related to each other.

The opposite effects of oxygen and ammonia upon a number of lines give a basis for separating a certain group from the main body of the spectrum. These lines are as follows:

5853.91	4525.19
4934.24	4166.24
4900.13	4130.88
4700.64	3906.20
4554.21	3891.97

A comparison of a large number of plates shows these lines in every case to be strengthened by oxygen and weakened by ammonia more than the remaining lines of the spectrum. Nitrogen produces scarcely any change from the appearance of the lines in air. A slight relative weakening sometimes appears, showing that the tendency of nitrogen is in the same direction as ammonia. Carbon dioxide gives a definite strengthening of these lines, comparable to that of oxygen. Both mercury vapor and sodium vapor strengthen the lines, the effect of the latter being almost as pronounced as that of oxygen. Copper terminals filled with barium salt also strengthen the lines as compared with barium in the carbon arc. With all these atmospheres, the most sensitive lines are those at λλ4166, 4525, and 4900. With the exception of λ3906, the group of lines given above are among the strongest in the spectrum, and are sharp with a moderate quantity of metal in the arc, though they broaden and reverse with a large quantity. They are, however, always different in appearance from the broad diffuse lines at λλ4323, 4325, 4489, and 4494, which are not affected by change of atmosphere. This greater sensitiveness of the sharper, more prominent lines of barium is similar to the effect of corresponding atmospheres upon the strontium spectrum, and unlike that upon the calcium lines. The changes in the line λ4525, as compared with its more diffuse companion λ4523, are very striking.

Looking now at the relations between these lines which are affected by surrounding atmosphere, we find that almost the

only definite regularity so far discovered in the barium spectrum is the existence of four pairs of lines with constant difference in wave number, as follows:

λ		Vibration-Difference
6497.07	- - - - - - - -	1691.05
5853.91		
4934.24	- - - - - - - -	1691.16
4554.21		
4900.13	- - - - - - - -	1690.90
4525.19		
4166.24	- - - - - - - -	1691.47
3891.97		

It will be observed that all of these lines occur in my list of sensitive lines, except λ6497, which is beyond the region covered by my photographs. My results for the barium spectrum, then, serve to separate these lines, together with a few others, from the main body of the spectrum, as forming a series of related pairs, which appear to be relatively strengthened by increased vapor density in the arc.

ZINC.

My data for the zinc spectrum cover only the region from λ3000 to λ4100 with a comparison of the effects of oxygen and air. Brass terminals were used for the arc, so that the stronger copper lines appear. My results show a decided strengthening in oxygen of the group of lines

3282.42	3345.13
3702.62	3345.62
3303.03	3346.04

belonging to the first subseries of Kayser and Runge.

The lines

3572.90	3740.12
3671.71	4019.75
3683.63	4058.02

between which no relation has been found, are weaker in oxygen than in air. The difference is not as great as in the case of the series group. This strengthening of the series lines by oxygen is similar to that observed with the series lines of calcium, while

the effect on the unrelated lines is like that which we shall see in the case of the line pairs of copper.

COPPER.

The spectrum of copper shows a large number of relative differences in intensities of lines, when different atmospheres are used around the arc, the most important changes being given by an atmosphere of oxygen. The copper arc in oxygen burns with difficulty and frequently goes out, in decided contrast to the behavior of the carbon arc in oxygen. This action may be due to the formation of a non-conducting coating of copper oxide on the terminal, though it is doubtful if this forms in the arc itself. The oxidation of copper is not accompanied by the increased heat and wasting of the electrodes which accompanies the formation of carbon dioxide in the carbon arc.

In general, the more diffuse copper lines are most reduced by oxygen, the best examples of this being the pairs of wavelengths

3247.65	3654.60
3274.06	3688.60

These pairs are almost blotted out by a strong current of oxygen. The strong pair λ4023 and λ4063 are weakened by oxygen, though not so much as the preceding; while many of the sharper lines are quite unaffected, notably those of wavelengths:

3308.10	4378.40
3599.20	4587.19
3602.11	4651.31

The lines from λ3100 to λ5300 most reduced by oxygen are as follows:

3194.17	3925.40
3208.32	4015.80
3247.65	4022.83
3274.06	4056.80
3337.95	4062.94
3384.88	4480.59
3530.50	4531.04
3654.60	5105.75
3688.60	5153.33
3825.13	5218.45
3861.88	

It will be observed that these twenty-one lines include those of the pairs given by Kayser[1] as belonging to the first and second subseries of copper; also the pair λ4015.80 and λ4056.80, and the strong pair λ3247.65 and λ3274.06 which Kayser thinks may be a member of the principal series of copper. The lines of these several pairs have nearly the same difference in wave-number (248). Besides these pairs we have a weakening by oxygen of the seven lines:

3194.97	3530.50
3208.32	3925.40
3337.95	5105.75
3384.88	

In addition to these known relations, I have found that a number of these lines affected in the same way by oxygen form pairs with a constant vibration difference of about 3400 as follows:

λ		Vibration-Difference
3247.65	- - - - - - -	3428.7
3654.60		
3274.06	- - - - - - -	3432.5
3688.60		
3384.88	- - - - - - -	3400.2
3825.13		
3925.40	- - - - - - -	3405.1
4531.04		

This gives an interesting relation between the pair λλ3247.65, 3274.06 and one of the pairs of Kayser's first subseries. The corresponding lines of these two pairs are seen to have nearly the same difference in wave-number. The two pairs of the second subseries have a line of each pair related to an outside line by this constant difference; but in one case it is the upper line of the pair which has an outside companion, and in the other case the lower line. The connection indicated by these constant differences does not appear to be a simple one. It is probably a result of some relation among the the vibrations giving rise to this set of lines which are affected in the same way by change of physical conditions.

[1] *Handbuch der Spectroscopie*, **2**, pp. 530–531.

The use of nitrogen gives effects but little different from those with air around the arc, except in the case of the pair λ3247.65 and λ3274.06. These are slightly weaker with nitrogen, and the reversal is narrower, while scarcely any change can be perceived in the other lines which are weakened by oxygen.

The effect of mercury vapor on the copper lines is similar to that of oxygen, the same lines being weakened, and to almost the same degree, as by a strong current of oxygen. The action is the same with sodium vapor around the arc, though not so pronounced, only the most sensitive lines being changed.

Mixtures of other vapors with that of copper were tried by using brass electrodes, giving strong zinc lines mixed with those of copper, and by using one copper and one carbon terminal, giving the carbon and cyanogen bands. These experiments were made with the arc in the open air. No relative differences could be detected in either case by comparing the plates with those taken with copper terminals.

Looking now to see if changes in vapor density would produce the effects we observe, the first fact to be noted is that the effect of oxygen upon the burning of the arc with copper terminals is very different from that when carbon electrodes are used. With carbon terminals, the arc burns with great vigor and brightness in oxygen, the carbons being rapidly consumed, probably with the formation of large quantities of carbon dioxide. With copper terminals, on the other hand, it is difficult to maintain the arc in oxygen. Some copper oxide is formed, but no change in the flame is observed except a weakening. A longer exposure is required for the same general intensity of the spectrum, as compared with the arc in air. This agrees with the observation of Porter,[1] who used the rotating arc with electrodes of magnesium, tin, zinc, and iron in oxygen, and found the metallic lines weakened. This difference between the carbon and metallic arcs must be considered in questions of vapor density.

The conditions with oxygen about the carbon arc appeared favorable for greater vapor density, and its action in intensifying certain lines strengthened the hypothesis that the change

[1] *Loc. cit.*

was produced by greater vapor density. With the copper arc, however, the weak action in an atmosphere of oxygen appears favorable for a low vapor density in the arc, and the reduction of the broad diffuse lines by oxygen can be attributed to this cause. Both mercury and sodium vapors weaken the arc. The action of sodium vapor is not the same as with the carbon arc. The current remains the same as with the arc in air, so that the sodium does not appear to increase the conductivity, and the arc burns with difficulty, frequently going out. Nitrogen might be expected to give little change of vapor density from that of air, and it is noted that only the most sensitive lines are changed by nitrogen, whose effect is slightly to reduce the vapor density, if my hypothesis is correct.

DISCUSSION OF RESULTS.

The first general result to be noted as given by a change of atmosphere around the arc is the power of the method as a means of separating the lines of an element into groups. The several groups may then be investigated with respect to series relations between the lines. It thus offers possibilities of finding new relations between lines, especially in the case of elements having so large a number of lines that it would be difficult to obtain a starting-point without some means of separating certain groups.

The magnetic field is a well-known means of separating lines into groups, and an interesting comparison of the two methods is given by comparing my results with those given by Kayser in his discussion of the Zeeman effect.[1] From this it will be seen that a number of lines in the spectra of calcium, strontium, barium, and copper, which belong to certain types in the classification of Zeeman phenomena, are among the lines which I find affected by a surrounding atmosphere differently from the other lines in those spectra.

The fact that a certain atmosphere may not produce the same effect on lines of the same kind (sharp or diffuse) in the spectra of different metals, might present a difficulty. Especially is

[1] *Handbuch der Spectroscopie*, 2, 671.

this the case with the behavior of calcium and strontium in the carbon arc. The structure of these two spectra show many similarities, yet the diffuse calcium lines belonging to Kayser and Runge's series are the more sensitive to change of atmosphere; while in the case of strontium, the strong lines not in Kayser and Runge's series respond most readily. It is very probable, however, that the groups of strong lines actually form the principal series in these two spectra, though no numerical relation has yet been found between the lines except the constant differences. If this is the case, the state of affairs seems to be that a change of atmosphere produces the greatest difference on the principal series of strontium and on the first subseries of calcium—an effect which might easily result from the differences between the two metals, in spite of their many similarities. The more rapid volatilization of the calcium salt in the arc might bring about a change of condition sufficient to account for the different behavior of the two series.

In regard to the probable action of the surrounding atmosphere in bringing about the changes in the spectral lines, the weight of evidence seems to indicate that chemical action has little or no part in producing the effects, except as it may affect the vapor density in the arc. The chief arguments against the effect of an atmosphere of oxygen being due to chemical action are (1) that the use of pure nitrogen produces little change as compared with the arc in air, and occasionally its action is in the same direction as that of oxygen; (2) that a cloud of sodium vapor around the arc leaves most of the lines unchanged, and slightly enhances those of one group, as has been noted in several cases.

The hypothesis that seems best to accord with my results and those of others is that the effects are to be ascribed to changes in vapor density which effect the vibrations producing the lines belonging to a certain group—vibrations which are probably similar in general character, judging from the behavior of the resulting spectral lines. This theory has been kept in view during the discussion of the results, and seems to be the one which best co-ordinates the various phenomena, both as to the

changes observed with different atmospheres, and those in which the supply of metal was varied with the arc in air.

It is possible that temperature changes may play a large part in giving the effects we observe, as the most distinct changes in the spectrum are associated with conditions which probably involve change of temperature in the arc. However, the facts that the carbon arc in oxygen does not give changes proportional to its probable change of temperature, and that these changes are brought about in some degree by other conditions which should not involve much change of temperature, point to the conclusion that temperature is not the direct cause of the effects observed, though it may assist in bringing about the state which is the actual cause. Temperature changes would be closely connected with changes in vapor density, to which it seems reasonable to attribute many of the results.

It is the writer's opinion that not enough attention has heretofore been given to the effects of changes in vapor density upon the intensities of lines. Is it not possible that density is the determining element for the relative intensities, as pressure seems to be for displacements and the use of the magnetic field for polarization properties? Any notions as to the action of change of vapor density in modifying the electrical properties of the vibrating particles must be entirely hypothetical, but it is easy to conceive that such actions might be selective in their nature, resulting in a change for only a portion of the lines.

Comparing my results with some observations of the spark spectrum which have been published, we find some striking evidences that the use of atmospheres which apparently give lower vapor density tend to make the arc spectrum similar to that of the spark discharge. Sir William and Lady Huggins [1] found that when the density of calcium vapor in a vacuum tube was decreased by gradually removing the calcium from the electrodes, the H and K lines, together with the pairs at λλ3737, 3706, and 3179, 3159 were weakened much less rapidly than the other lines and finally were the only lines visible. These are the lines which I find but slightly altered by changes in vapor

[1] Astrophysical Journal, 6, 77, 1897.

density in the arc. Similarly, the photograph of the spectrum of the spark discharge in calcium vapor given by Eder and Valenta[1] shows the lines λλ 3737, 3706, 3179, 3159 to have many times the intensity of λλ 3644, 3630 and the other series lines in that region. This state is approached by some of my photographs taken with the arc in ammonia, which appeared to give the lowest vapor density of the gases I have used. Again, the table given by Eder and Valenta,[2] in which their measurements of the spark lines of copper are compared with those of Kayser and Runge for the arc, shows that if the standards of intensity adopted by the two pairs of observers are at all alike, then most of the lines which I find weakened by an atmosphere of oxygen around the copper arc are much weaker in the spark spectrum than in that of the arc.

If, as is very probable, the vapor density in vacuum tubes and in the spark discharge is much less than that in the electric arc, we may arrive at a simple explanation of the action of hydrogen in intensifying certain spark lines, as observed by Crew and Porter. As the hydrogen atmosphere around the metallic arc seems to have much the same action as ammonia in causing the arc to burn with difficulty, probably reducing the vapor density, we are led to the idea that those lines which appear strongly in the spark, and faintly or not at all in the arc, may be lines whose vibrations require a low vapor density. The action of hydrogen in strengthening such lines in the arc would then be explained by the reduction of the vapor density, thereby bringing the conditions of the arc to approach those of the spark.

Further evidence in support of this view is given by the work just published by Hartmann,[3] who finds λ 4481, as given by the arc between magnesium terminals, much increased in intensity when a current as small as 0.4 ampere is used, the arc being constantly interrupted, with only a slight heating of the terminals and little vaporization—conditions which should give a low vapor density. The results show a similarity to the

[1] *Denkschriften der K. Akademie der Wissenschaften zu Wien*, **68**, 534, 1900.

[2] *Ibid.*, **63**, 189, 1896.

[3] ASTROPHYSICAL JOURNAL, **17**, 270, 1903.

spark spectrum and to the effects given by the arc when surrounded by atmospheres which should give low vapor density.

My results, then, considered in connection with those of others, show a definite selective action in the effects of surrounding atmospheres on spectral lines—an effect evidently connected with the series relations of the element. All of the results point to a change of vapor density in the arc as the direct cause of the effects observed. The tendency of a low vapor density seems to be to make the arc spectrum more like that of the spark.

In conclusion, I wish to express my thanks to Professors Slate and Lewis for constant interest in the work and many helpful suggestions.

UNIVERSITY OF CALIFORNIA,
Berkeley, May 1903.

ON THE SPECTRUM OF THE SPONTANEOUS LUMINOUS RADIATION OF RADIUM AT ORDINARY TEMPERATURES.[1]

By Sir William Huggins and Lady Huggins.

The discovery of an element possessing such remarkable and novel properties as radium, which in its separate and distinct form as a new chemical element we owe to the researches of Professor and M^me^ Curie, has already thrown many beams of suggestive light into the very obscure regions of the constitution of matter. In radium we have a body which appears to be spontaneously and without ceasing giving off energy in several forms. According to Professor Rutherford,[2] following upon the work of Becquerel, M. and M^me^ Curie, and others, the emanations going off from radium are at least of three kinds: first, an emanation of heavy corpuscles, larger in mass than the hydrogen atom, moving with a high velocity, and carrying a positive charge; secondly, of negatively charged electrons which form a powerful and penetrating cathode emanation;[3] and, further, of a radio-activity which diffuses from the radium as if gaseous in its nature. In addition, M. and M^me^ Curie have found that radium spontaneously maintains a temperature about 1°.50 C. above the surrounding temperature, and therefore emits heat radiations of wave-lengths falling within the infra-red part of the spectrum.

Now, in addition to these forms of radiant energy, the glowing of radium in the dark shows that it emits a luminous radiation

[1] From advance proofs of an article to appear in the *Proceedings of the Royal Society*.

[2] *Phil. Mag.*, (6) **5**, 445, 561, 1903.

[3] As an illustration of the penetrative power of the radio-active effects of pure radium bromide, the following experience may be recorded here. About 1 centigram of radium bromide (Buchler & Co., Brunswick) had been placed in an upper drawer of my writing table, while in a lower cupboard of the same table was a store of photographic plates. After a week or two, all the plates, in boxes lying upon each other three or four deep, were found to be as completely fogged as if they had been exposed to light.

spontaneously at ordinary temperatures. It appeared to us probable that in this glow we had not to do with either phosphorescence or fluorescence as usually understood, but with an independent and continuous radiation set up by those more active molecules which are supposed, in consequence of a condition of internal instability, to be the source of all the phenomena of radio-activity, and which can scarcely fail themselves to be violently agitated, in connection with disruptive molecular changes—especially the flinging off of the heavy corpuscles—during which, part of the energy stored up within the molecule is liberated in the kinetic form.

Taking this view of the luminous radiations visible to the eye, it seemed highly probable that the molecular motions by which they were set up, whether we suppose all the radium molecules alike to be concerned, or those only which are in active change, would be so far analogous to the vibrations produced artificially, when radium vapor is rendered luminous in a flame, or by the blow of an electric discharge, as, in like manner, to set up radiations of certain definite wave-lengths or, in other words, to furnish a spectrum of bright lines.

A preliminary prismatic examination of the glow from pure radium bromide was attempted by eye. In consequence of the feebleness of the light under dispersion a slit spectroscope could not be used. A thin fragment of some length of radium was selected, which in the dark shone as a narrow line of light; when this was viewed through a direct-vision prism, it was seen to be dispersed into a spectrum which extended from the blue down to about D, where it became too faint to be traced farther in the direction of the red. Within this faint spectrum certain spots were distinctly brighter, due, in all probability, to the presence of bright lines at those positions in the spectrum.

The success of this preliminary observation encouraged us to hope that it might be possible by availing ourselves of the accumulative power of continuous photographic exposure, to obtain a record of the blue, violet, and ultra-violet regions of the spectrum, if the glow radiations extended so far.

We made use of a small quartz spectroscope which had been

constructed some years ago for very faint celestial objects. It consists of a compound quartz prism of 60°, consisting of two prisms of 30° of right-handed and left-handed quartz respectively. The quartz lenses are of short focus and of large angular aperture, being about $f = \frac{1}{3}$. The focal length of the lenses is $5\frac{3}{4}$ inches; they are plano-convex, the marginal parts of the convex surfaces being "figured" to diminish spherical aberration.

The solid radium bromide was placed at about a millimeter distance in front of the slit, which had to be wider than if a bright object was being photographed; the width was about $\frac{1}{450}$ inch. In the case of the spark spectrum of radium and the comparison spectrum of nitrogen, a slit of less than half this width was used.

With the exposure of twenty-four hours, faint traces of two lines were seen on the plate. After several trials the negative reproduced on the accompanying plate was obtained with an exposure of seventy-two hours. The reproduction is enlarged two and a half times. The spectrum consists of eight bright lines, and at least eight faint lines, together with a faint trace of continuous spectrum in the blue region, which does not come out in the reproduction.

In consequence of the wide slit and the small scale of the spectrum, it is not possible to measure with certainty to the fourth figure, but the probable error is, we think, not greater than two units in the fourth place.

It was seen at once that the two very strong characteristic rays of the spark spectrum of radium, in this part of the spectrum, namely, λ 3814.5 and 3649.6[1] were not present on the plate. It was clear that the spectrum was not of the radium molecule when excited by the electric discharge. It was indeed not improbable that if the radiation came alone from the most active molecules, which were suffering loss by material emanations, then, if we may accept the analogy from sound, like a filed tuning-fork they would no longer give radiations of the same wave-lengths as before.

[1] For spark spectrum of radium, see DEMARÇAY, *Comptes Rendus*, **129**, 786, and **131**, 258; Exner and Haschek, *Wien. Akad. Sitzber.*, **110**, July 1901; RUNGE, ASTROPHYSICAL JOURNAL, **12**, 1.

On comparing the new spectrum with the band spectrum of nitrogen, seven of the strongest lines were found to agree, not only in position, but also in intensity, and in character with those of the three nitrogen bands in this part of the spectrum.

The positions of the three bands are, according to Ames,[1] λ3576.85, 3371.2 and 3158.9.

Indications of other lines, besides those which can be seen in the reproduction, can be faintly glimpsed on the negative. There seems little doubt that with a longer photographic exposure a more complete spectrum will be obtained. We have now secured some radium bromide prepared by the Société Centrale de Produits Chimiques, and it is our intention to take photographs of this salt as well as photographs of the German salt with longer exposures. It may then be that indications of helium, and possibly of radium itself, may be forthcoming.

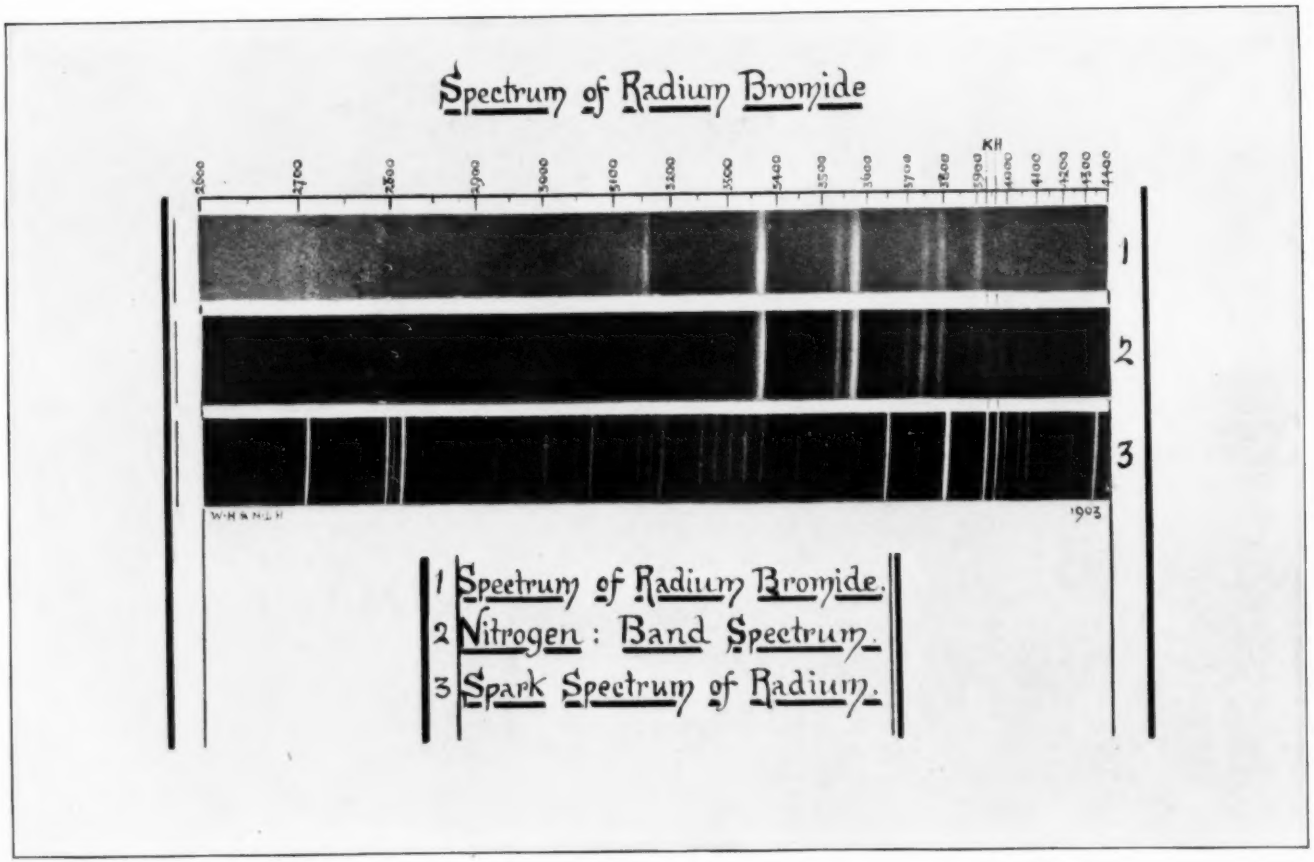
Nearly the whole of the ultra-violet radiations appear to come from nitrogen, and we think it best to refrain from any discussion at this moment. Have we to do with occluded or with atmospheric nitrogen? The remarkable fact should be pointed out that in radium we have a body which at the ordinary temperature sets up radiations which are similar to those which have hitherto only been obtained in connection with the electric discharge.

Description of the plate.—At the top is placed a scale of approximate wave-lengths. Immediately below is a reproduction, enlarged two and a half times, of the spectrum obtained from the radium bromide with an exposure of seventy-two hours. As has been already explained, this has been shifted to bring the lines into position with those of nitrogen photographed from a vacuum tube. The identity of the two spectra seems complete. The third band is faint in the nitrogen spectrum on account of the absorption of the glass of the tube.

Below is a spark spectrum of radium bromide from the Société Centrale de Produits Chimiques. The H and K lines of calcium are present, as well as faintly some of the stronger lines of barium. The characteristic lines of radium at λ3814.59 and

[1] *Phil. Mag.*, (5) **30**, 57, 1890. See also DESLANDRES, *Comptes Rendus*, **101**, 1256; and PERCIVAL LEWIS, ASTROPHYSICAL JOURNAL, **12**, 8.

PLATE IV.


Spectrum of Radium Bromide
KH
2600
2700
2800
2900
3000
3100
3200
3400
3500
3600
3700
3800
3900
4000
4100
4200
4300
4400
1
2
3
1903
1 Spectrum of Radium Bromide.
2 Nitrogen : Band Spectrum.
3 Spark Spectrum of Radium.

3649.7 come out strongly, as well as the strong line recorded by Demarçay at λ4340.6. A strong line about λ2710 was placed by Berndt[1] at λ2708.6. The strong line a little beyond, about λ2814 is due to radium. We do not recognize several lines recorded by Exner and Haschek[2] in this part of the spectrum.

[1] *Phys. Zeitschr.*, **2**, No. 12 (1900–1).

[2] *Sitzb. Ak. Wiss. Wien.*, **110**, July 4, 1901.

Reviews.

Problems in Astrophysics. By Miss A. M. Clerke. London: A. & C. Black, 1903.

It is not possible to separate entirely the child Astrophysics from the parent Astronomy. The two are mutually dependent in much of their instrumental equipment and in many of their methods, and their results are often intimately related. Radial-velocity determinations, for example, are based largely upon astrophysical methods, but the direct results are mostly astrometrical. However, the newer term serves an exceedingly useful purpose, and has become permanently fixed in our literature. In general, we may say that the older astronomy is concerned with the determination of the structure of the sidereal universe; with the arrangement of the sidereal units in space, and with their motions and relations in accordance with Newton's law of gravitation. Astrophysics, on the contrary, is interested in determining *what the stars really are*, and what the history of their development has been.

The beginning of astrophysical inquiry is old, but until the last half-century its results were surprisingly few. Theories of planetary evolution by Kant and Laplace, the observations and wonderfully sagacious deductions of the elder Herschel, and studies of planetary conditions and of Sun-spots, constituted the main body of the science up to 1859. But the spirit of inquiry as to the nature and history of the heavenly bodies was latent in many quarters; and Kirchhoff's superlatively important discovery that "the light which reveals to us the existence of the heavenly bodies also bears the secret of their constitution and physical condition," opened a gateway to Comte's forbidden field which many were ready to enter. The pioneer work of Secchi, Huggins, Vogel, Young, and their colleagues in the next quarter-century was very fruitful. Their results, originally scattered through the journals, were collected and systematized by Roscoe, Schellen, Kayser, and later by Scheiner and Clerke;[1] but the speed of development in the past fifteen years has been such that astrophysical literature is again widely scattered. This statement will not, I trust, be con-

[1] Miss Clerke, *The System of the Stars*, 1890.

strued into an overlooking of the colossal work on general spectroscopy now issuing from the able pen of Professor Kayser. A historical and critical survey of astrophysics is greatly needed, and the appearance of Miss Clerke's volume could scarcely have been better timed.

The author's intention, as announced in the preface, "is not so much to instruct as to suggest. It represents a sort of reconnaissance, and embodies the information collected by scouts and skirmishers regarding practicable lines of advance and accessible points of attack. . . . . Before attempting to add to our store of learning, we must realize what is already possessed." This statement of purpose has been consistently adhered to. By way of suggestions for future lines of research this book is the richest one known to me.

The physical study of the Sun forms the basis of astrophysical research more fully perhaps than astronomers themselves have realized. It is the only star near enough to be studied in some geometrical detail, all other stars giving integrated images which practically are mathematical points. It is likewise the only star bright enough to supply satisfactory metrical standards demanded in the study of other stars. Miss Clerke devotes the first third of the volume to a treatment of the Sun. After outlining "The Progress of Solar Physics," there are chapters on "The Chemistry of the Sun," "The Reversing Layer," "The Photosphere," "The Sun-spots," "The Faculæ and Prominences," "The Chromosphere," "The Corona," "The Sun's Rotation," "The Solar Cycle," and "The Sun as a Whole."

The difficulties of solar study, in spite of comparative nearness and intense brightness, are very great. It is not generally appreciated that we are unable to study the body of the Sun, except by very indirect methods. Its interior is invisible; the photospheric veil hides it completely from view. The photosphere, chromosphere, prominences, corona, etc.—the only portions accessible for direct observation—are an insignificant part of its mass. They are literally the Sun's outcasts. Our knowledge of the Sun as a whole is based almost entirely upon a study of these outcasts. We might hope to reach safe conclusions as to the characteristics of a hermit nation by making a careful study of its banished subjects, provided the observed types correspond with types produced by our own civilization; but if new types, new customs, new forms, presented themselves on a stupendous scale, and were observable only at long range, our conclusions as to the country from which they were expelled should come slowly and uncertainly. It is difficult to say what the chromosphere is. To determine what the conditions

within the body of the Sun must be in order to create and maintain such an outcast shell is far more difficult.

Again, the ordinary photographic or visual image of the Sun is an integrated one. A coronal photograph secured at a total eclipse is the result of a projection upon and into one plane, at right angles to the line of sight, of all that remains of the Sun after subtracting the (approximate) cylinder of matter hidden by the Moon. The tops of some coronal streamers, the intermediate portions of others, the bases of those near the limb, the corresponding parts of prominences and chromosphere, are all projected into one point, illuminated in part by reflected and in part by inherent light. Whether every man who has gone forth to solve the riddle of the corona has fully realized the odds against success is doubtful.

Imperfections in atmospheric conditions are perhaps more liable to introduce uncertainties in solar observations than in any other class. Whether Janssen's *réseau photosphérique* phenomena are of solar or terrestrial origin is still uncertain, as Miss Clerke states on p. 17, but Hale's recent results with the spectroheliograph, in which the image is built up from one limb to the opposite limb in some two or three minutes, confirm the pretty general belief that the effect is purely terrestrial.

The impossibility at present of reproducing solar phenomena in our laboratories is recognized as our most severe limitation. There is scarcely one result to be obtained by interpolation : extrapolation is demanded everywhere, and at great distances beyond the range of observed points in the curves. Such decided extensions of our resources as the electric furnace provides seem at best but beginnings toward what is required. And, as Miss Clerke repeatedly points out, our knowledge of the effect of the presence of one vapor upon the spectrum of another vapor is almost wholly wanting. Evidence is not lacking, however, that such effects must be both common and potent.

There can be no doubt that the Sun is a very tempestuous body. It is probable that convection currents are on a scale so great and have at times a speed so high that we have difficulty in adequately realizing their immensity. I fear, therefore, that Miss Clerke's division of the solar outcasts into "several distinct envelopes" overlying the photosphere (p. 16) — reversing layer, chromosphere, corona, etc. — is somewhat too definite, even with her qualifying remark that none of them is "apparently in a condition of atmospheric equilibrium." Our direct evidence of disturbance in the photosphere is limited largely to the

visible spots, but the faculæ and prominences are almost certainly the results of disturbances generally invisible. In this connection it would be well, I think, to modify the statement on p. 74, "but faculæ exist abundantly where there are no spots," to read where there are no visible spots. Faculæ accompany very small spots as well as large ones. It is natural that there should be countless invisible spots, and that they as well as the large ones should be surrounded by faculæ. Spots one second of arc (650 kilometers) in diameter could easily escape notice. There is little doubt that the coronal streamers springing from every part of the sphere are produced in some way by powerful but invisible disturbances in all parts of the surface. There is certainly a close relation between spots and faculæ, and the latter are not confined to the spot zones; between chromosphere and prominences; and between prominences and at least the inner part of the corona. The tremendous cone of disturbance in the corona of 1901 (Sumatra) and in its apparent situation immediately above the large, and only Sun-spot visible near that date, discovered by Perrine[1] — perhaps inadvertently not mentioned in *Problems in Astrophysics* — is also very significant. Not to dwell on the details longer, it seems to me that the strata above the photosphere must be highly confused, though there is no doubt that the order of elevation generally assigned to the reversing layer, chromosphere, etc., is correct. If the zeal displayed by a successful comet hunter were devoted to searching for changes in the solar spectrum, rich rewards could reasonably be expected.

These statements are not opposed to the fact that progress must be made by differentiating and isolating various kinds of phenomena; and those instruments and methods which have this power most markedly are the most promising. The spectrographic method of differentiating, including the line-displacement principle, has had no equal; and the extension of it by the two-slit spectroheliograph has been a real advance. Much can reasonably be expected from Hale's improved form of this instrument.

The value of a solar eclipse as a partial differentiator, through the elimination of photospheric light, should not be overlooked. Surprising, indeed, is the impetus given to solar study by eclipse observations. Our knowledge of the *existence* of the reversing layer, the chromosphere, the prominences, and the corona, is an eclipse product; and so are many of our present everyday methods of studying them. The

[1] *Lick Observatory Bulletin* No. 18, and CLERKE'S *History of Astronomy*, 4th ed., p. 190.

richness of eclipse results, considering the remarkably short intervals available for observation, is unique in science. Nor are eclipse problems all solved; every such event brings its returns. Whether the reversing layer and chromosphere can ever be studied equally well without an eclipse is a question. They probably cannot, by means now available, but Hale's observation of carbon bright lines near the photosphere shows clearly that the effort should be made. Limitations in quality may be more than balanced by continuity and timeliness. The reviewer agrees with Miss Clerke (p. 135) that "the prospect is dim of realizing" success in observing the corona without an eclipse, at least along the lines of attack thus far attempted. Any chance for even moderate success would seem to be limited to the gaseous inner portion, and a daily record of this would no doubt be extremely valuable, but the real problem of the corona would remain unsolved.

Miss Clerke refers to the possibility that electrical or magnetic forces are playing prominent parts in solar and stellar phenomena; and while positive evidence of their action has not yet been recognized, the idea is a valuable one, and observers would do well to apply tests for Zeeman and other effects whenever opportunity offers. In this connection, I have been more than surprised to find no mention of Arrhenius's theory of light- and heat-pressure effects in the production of the more extended solar phenomena. Nichols's proof that theory is in agreement with observation on this question requires us to consider whether such forces at the Sun's surface may not be sufficient to create observable movements of finely divided matter existing at photospheric temperatures. Is it not possible that the resultant of gravity and light- and heat-pressures is small for very minute particles, and that herein lies the explanation of the hypothetical principle of "levity" referred to by the author, on p. 51 and elsewhere?

The salient points in solar progress have received masterful treatment from Miss Clerke. Especially well is attention called to the gaps in our knowledge. Many of them could be filled, at least in part, by the energetic use of apparatus now in existing observatories, while others demand new and expensive equipments, with ample provision for their systematic application. The Sun as the great exemplar of our science is receiving but scant attention.

Part II, 375 pages on "Sidereal Physics," is a very able presentation of facts and theories for all known types of stars, and for nebulæ. It is not so systematic as the author's treatment of "Solar Physics," but the nature of the subject, and the scattered character of observed

facts, forbid. There are chapters on all the principal spectrum types, on all the types of variable stars, on all known classes of nebulæ, on the spectra of double stars, on spectroscopic binaries, new stars, dark stars, and the Milky Way, etc.; forty-one chapters, each rich with the most salient facts of observation, with theories very wisely and conservatively discussed, and with constant suggestion as to points most in need of strengthening by observation. The impossibility of doing justice to so extensive a work in a brief review will be evident to all.

The field of stellar and nebular investigation has its own difficulties. The quantity of light received from a star or nebula is really very minute; a stellar spectrum is an integrated result, for photosphere, reversing layer, chromosphere, prominences, and corona—all fall in one small point, as viewed from the Earth; the distances, diameters, and in nearly all cases the masses, are unknown, leaving us without basis for correlating masses, quantity, and intensity of light; the amount of measurement accurate according to today's standard is small; little effort has been devoted to the ultra-violet region, so important from temperature considerations; and laboratory accompaniments are but just beginning on a requisite scale. Nevertheless, the mass of solid fact brought within the realm of knowledge in the past forty years is exceedingly encouraging.

The foundation of every philosophic treatise on the stars must rest, so far as information now avaible is concerned, upon a classification of stars according to spectral types, preferably in the order of their supposed evolution from nebulæ to dark stars. Miss Clerke treats nebulæ last of all. This is not the order of nature, but the plan has its advantages, principally because we know too little about the nebulæ and their processes of transition to stellar states. The astrophysical treatise of the future will probably begin with the nebulæ—or perhaps with the origin of the nebulæ! Miss Clerke assigns all stellar spectra to eight classes: four showing absorption spectra only, and four marked by both absorption and emission spectra. The first five classes are: I, helium stars, brilliantly white, hydrogen and helium absorption predominating, the *Orion* and *Pleiades* stars as illustrations; II, hydrogen stars, with intense hydrogen absorption, feeble and thin calcium H and K, feeble iron lines, with *Vega* and *Sirius* as examples; III, solar stars, with innumerable metallic lines, the lower hydrogen lines, and broad and heavy H and K, with the Sun and *Arcturus* as types; IV, stars with fluted spectra, containing a great number of fine dark lines, with superposed heavy absorption flutings whose heads are toward

the violet, α *Orionis* and α *Herculis* as illustrations; V, carbon stars, with innumerable dark lines, very feeble in violet, strong carbon absorption flutings and many apparent bright lines, 19 *Piscium* being typical.

This scheme of classification differs very little from Secchi's four-type system. Classes I and II are subdivisions of Secchi's Type I. Class III is Secchi's II, and IV and V are Secchi's III and IV. It is in effect, also, a condensation of Miss Maury's system of more than twenty groups. It is of course understood by all readers that any such scheme of classification will divide the stellar spectra into compartments only very imperfectly: there will be many spectra on the border lines between classes, especially in Classes I, II, and III. Classes IV and V have more individuality than the others.

Secchi's classification has been a most fortunate and useful one. For general purposes it is satisfactory even today, when the observational data are almost incomparably more numerous and accurate than when Secchi formed it; and I doubt whether the time has come to replace it with another. The Harvard system is very useful, and perfectly justifiable, as an expression of the results of systematic examination and study of a great number of spectra. But its general adoption in the daily work of astrophysicists would seem to be unwise for the present, in view of our very imperfect knowledge of the temperature and other basic conditions underlying the real system of stellar development. New determinations of the spheroidal constants of the Earth, or of the aberration constant, based upon the latest data, are extremely valuable; but to adopt each improved spheroid as a basis for government surveys, or each improved aberration constant in astronomical yearbooks, would lead to hopeless confusion. For similar reasons I regret the division of Secchi's I into Miss Clerke's I and II, and the mechanical shifting of the former's II, III, and IV to the latter's III, IV, and V. The highly desirable distinctions which Miss Clerke desired to call attention to in stars of Secchi's I could have been accomplished more wisely, I think, by some subclassification analogous to Vogel's — notwithstanding the very important calcium-absorption distinctions covered by her plan. Again, her Class VI stars, having fluted spectra and showing hydrogen and other bright lines, includes only the variables of the *o Ceti* type. They are certainly very closely related to her Class IV stars. The spectra of the variables apparently differ from those of Class IV only in having bright lines, induced probably by the forces which produce variations

in brightness; and in this case a subclass of IV would certainly be satisfactory and more logical. Helium stars with bright lines and Wolf-Rayet stars are assigned to Classes VII and VIII. Miss Clerke states that "no hypothesis of growth and affinity is implied by the order of succession given to the bright line objects," though "it certainly rests upon broad and unmistakable distinctions." Class VII is certainly closely related to the Class I helium stars, and a subdivision for these under I would seem to me both advantageous and natural. Of their close relationship there is no doubt, and many facts could be cited in that connection. Space prevents reference to more than the bright lines in spectra of *Alcyone*, *Pleione*, μ *Centauri*, etc., and the absence of the bright lines from many otherwise almost identical spectra of Class I. The assignment of a special class to the Wolf-Rayet stars — Miss Clerke's VIII, Pickering's V — seems necessary at present, as no one is now able to fix their relation to other spectra. These stars, like comets, seem to stand out from any system of stellar evolution, but we should be fully justified, I think, in saying that they are comparatively new stars. It is also possible that they, as well as other stars of peculiar spectral types, are alien to the main sidereal system, and have no place in the sequence of development of ordinary stars; but this seems very improbable.

In the absence of full information as to what conditions produce bright lines in stellar spectra — whether in γ *Cassiopeiae* or in o *Ceti* — it is difficult to say why certain stars have bright lines and others have not. It is a constant surprise to me that bright-line spectra are not vastly more numerous than we have found them to be. Miss Clerke's reference to Classes I and II as *unveiled*, in contradistinction to the Sun's photospheric veil, may prove to be a very useful one. It probably has a basis in fact, though of this we have no positive proof. It would be surprising if the formation of bright lines is not favored by the absence of a photospheric veil. The study of bright-line spectra is one of the most fascinating and important subjects in spectroscopy. They appear to represent critical periods in stellar development, or to accompany rapid changes, as in variable stars. Systematic study of such spectra is greatly needed. The field is undoubtedly a rich one. It is but a few years since the discovery was made of both bright and dark lines of hydrogen in the same spectrum, the bright lines growing weaker from red to violet, and the dark lines growing stronger. Enough additional evidence has been collected to indicate that a general principle is here involved; and Kayser's explanation, or some other equally

simple one, will probably establish its fundamentality. As a case in point, since Miss Clerke wrote (p. 220), "the invisibility (up to the present) of hydrogen in the carbon stars is not easily accounted for," a long-exposure spectrogram secured with the Yerkes two-foot reflector has shown strong dark $H\gamma$ and $H\delta$ lines in the red star 19 *Piscium*, whereas $H\beta$ is bright or missing in all observed stars of that type. The laboratory investigations of Hale and others on spark spectra obtained under high pressure show somewhat analogous phenomena, but of their correct interpretation I do not feel sure.

It is very unfortunate that our knowledge of temperature relations in stars of various types is so defective. The paucity of laboratory results is perhaps the major cause. The great importance and attractiveness of work along this line is evident to those who have followed investigations on the magnesium line at $\lambda 4481$ by Scheiner, Huggins, and others, or on the relation between arc and spark spectra by Hartmann. Very few such researches are sufficient to modify greatly our views on stellar temperature relations.

In this connection, attention should be called to the great need for extensive observations of stellar ultra-violet spectra, along the lines pointed out by Huggins. If the truly continuous portion of the ultra-violet in solar types is relatively stronger than in helium stars, that surprising fact should be fully established.

Miss Clerke's computations for the masses and radiative powers of various stars, leading to results very widely different from those for our Sun, are extremely interesting, and they in a sense mark the opening of a new field of great significance. Unfortunately, the available parallaxes for many of these stars are so uncertain as to introduce large uncertainty into her numerical results. The need for better and more numerous parallax data is at least as pressing in astrophysics as in the study of the distribution of the stars in space, and it is fortunate that extensive plans are forming at several observatories to supply the deficiency. However, granting the sufficiency of the author's parallax data, the tremendous radiative powers arrived at for certain stars need not wholly surprise us. There are certainly no more startling facts in all astronomy than those of *o Ceti* varying in brilliancy four-thousand-fold, with very little change in spectral type; of *Nova Cygni* varying from third to fifteenth magnitude, the spectrum at the present lower limit being continuous, without any evidence of bright lines; and of *Nova Persei* decreasing from the first in brilliancy in the northern hemisphere to below the tenth magnitude. In these cases the ratio of mass

to quantity of light radiations has had a remarkable range. It is impossible to say what the brightness of the Sun would be if its photospheric veil were suddenly removed.

Among the most interesting chapters in the book are those on variable stars. Excepting the new stars, a half-dozen *Algol* and δ *Cephei* types, *β Lyrae* and *o Ceti*, our knowledge of variable star spectra is remarkably slight. No well-equipped observer has devoted himself entirely or in the main to that subject. They offer a great variety of phenomena, and afford almost exclusive opportunities to observe spectral changes in rapid progress. Miss Clerke emphasizes the need for more work. There is in my opinion no richer field awaiting systematic cultivation. The number of variables known is about 1200.

The author's urgent recommendation that the bright lines in variable star spectra be tested for Zeeman effect is timely. The reviewer has held the subject in mind for several years in connection with the triple $H\gamma$ and $H\delta$ of *o Ceti*, but when the star was in favorable position the lines have been either single or too faint for such observation. The Lick tests on the broad bands of *Nova Persei* in 1901, and of *Nova Geminorum* in 1903 — no decrease in width resulting from a rotating Nicol prism — seem to be the only applications of such tests to stars thus far made.

Many interesting features of variable- and double-star spectra, of nebulæ, star clusters, etc., merit the reviewer's attention, but lack of space prevents.

In a book written in so broad a spirit, it would be invidious for the reviewer to enumerate the fifteen or twenty minor errors noticed, but a few should be referred to. On p. 500, Keeler's result is misinterpreted — that in the hydrogen vacuum tube "the third line ($H\gamma$) always vanishes experimentally before the first ($H\alpha$), while in a nebula it ($H\gamma$) shines unfailingly, although $H\beta$[1] be imperceptible." The $H\beta$ is, I think, visually much brighter in all nebulæ than is $H\gamma$, though $H\gamma$ is brighter than $H\alpha$. Again, at the top of p. 501, the uninformed reader will undoubtedly credit the discovery of variations in the relative intensities of the *Orion* nebular lines to one of the several observers who confirmed, and not to the discoverer who bore the brunt of the unusually hostile criticisms following the announcement of his discovery.

On p. 394, l. 13, the erroneous dates "7th and 13th November"

[1] Since this review has been put in type, it seems probable that $H\beta$ in the quotation is a misprint for $H\alpha$. — W. W. C.

instead of the correct dates 9th and 13th, are extremely unfortunate, though the dates were stated correctly in the author's *History of Astronomy*, 4th ed., p. 401.

It is to be regretted that the illustrations of nebulæ, clusters, etc., are not the most modern obtainable.

Miss Clerke's book is in my opinion most ideally planned: its history is fairly, but inconspicuously, complete; only relevant facts are stated; theory has not run away with observation; the defective corners in our field of knowledge are pointed out; the style is lucid, attractive, and logical; and to me its most remarkable feature is the wonderfully correct estimate of the relative values of observations, by an author with little or no experience in making observations.

W. W. CAMPBELL.